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(54) METHOD FOR CLEANING EXHAUST AND APPARATUS THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for cleaning exhaust by which NO_x and PM can be continuously self-removed under ordinary burning conditions without requiring specified control and to provide an exhaust cleaning catalyst and an apparatus for cleaning exhaust.

SOLUTION: In the method for cleaning exhaust, PM particles and NO_x in exhaust are removed by converting the PM particles to HC by a reaction represented by the formula $mC+nH_2O \rightarrow H_2nC_m+n/2.O_2$. The apparatus for cleaning exhaust has a filter obtained by carrying a noble metal and fine oxide particles of $\leq 1 \mu m$ average particle diameter on the inner walls of pores in a monolithic filter and disposed in an exhaust flue. In the method for cleaning exhaust, hydrogen generation reactions represented by the formulae $C+H_2O \rightarrow H_2+CO$ and $C+2H_2O \rightarrow 2H_2+CO_2$ are carried out at $\leq 500^\circ C$ exhaust temperature. The exhaust cleaning catalyst contains an H₂ generation catalyst and an NO_x removal catalyst, the H₂ generation catalyst contains Rh-carrying porous particles and metals such as Fe, Co, Mn and Ni, and these metals are contained at a ratio of 0.1-10 when Rh is represented by 1.

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CLAIMS

[Claim(s)]

[Claim 1] It is the approach of purifying the party curate particle and nitrogen oxides under exhaust air, and is the following reaction formula 1. $mC + nH_2O \rightarrow H_2nC_m + n/2 O_2$ -- (1)

The exhaust air purification approach characterized by including the process in which come out and a party curate particle is changed into a hydrocarbon by the reaction expressed.

[Claim 2] The above-mentioned hydrocarbon is made to react with nitrogen oxides, and it is the following reaction formula 2. $H_2nC_m + 4NO \rightarrow 2N_2 + mCO_2 + nH_2O$ -- (2)

The exhaust air purification approach according to claim 1 characterized by including the process out of which it comes, and which is changed into nitrogen, a carbon dioxide, and water by the reaction expressed.

[Claim 3] The exhaust air purification approach according to claim 1 or 2 characterized by performing the reaction expressed with the above-mentioned reaction formula 1 at the temperature of 350 degrees C or less.

[Claim 4] The exhaust air purification approach according to claim 3 characterized by performing the reaction expressed with the above-mentioned reaction formula 1 at the temperature of 280 degrees C or less.

[Claim 5] The exhaust air purification approach given in any one term of claims 1-4 characterized by performing the reaction expressed with the above-mentioned reaction formula 2 at the temperature of 350 degrees C or less.

[Claim 6] The exhaust air purification approach according to claim 5 characterized by performing the reaction expressed with the above-mentioned reaction formula 2 at the temperature of 280 degrees C or less.

[Claim 7] It is equipment which purifies the party curate particle and nitrogen oxides under exhaust air using the exhaust air purification approach of a publication in any one term of claims 1-6. At least one sort of noble-metals components chosen from the group which changes from platinum, palladium, and a rhodium to the pore wall of a monolith type filter, The exhaust emission control device characterized by arranging in an internal combustion engine's exhaust air gas duct the filter with a catalyst function with which a mean diameter supports at least one sort of oxide particles chosen from the group which consists of the alumina which is 1 micrometer or less, a titania, a zirconia, and a silica, and changes.

[Claim 8] The exhaust emission control device according to claim 7 characterized by the mean particle diameter of the above-mentioned oxide particle being 0.6 micrometers or less.

[Claim 9] The exhaust emission control device according to claim 7 or 8 characterized by for the porosity of the above-mentioned monolith type filter being 30 - 80%, and an average pore diameter being 5-40 micrometers.

[Claim 10] An exhaust emission control device given in any one term of claims 7-9 characterized by dividing the above-mentioned filter with a catalyst function into two or more steps, arranging it at a serial, and changing.

[Claim 11] The exhaust emission control device according to claim 10 with which pressure loss of the filter with a catalyst function of the exhaust air upstream is characterized by being larger than the pressure loss of the filter with a catalyst function of the exhaust air downstream.

[Claim 12] The exhaust emission control device according to claim 10 or 11 with which the average

pore diameter of the filter with a catalyst function of the exhaust air upstream is characterized by being larger than the average pore diameter of the filter with a catalyst function of the exhaust air downstream.

[Claim 13] An exhaust emission control device given in any one term of claims 10-12 to which the porosity of the filter with a catalyst function of the exhaust air upstream is characterized by being larger than the porosity of the filter with a catalyst function of the exhaust air downstream.

[Claim 14] An exhaust emission control device given in any one term of claims 10-13 to which the filter with a catalyst function of the above-mentioned exhaust air upstream is characterized by having a collision filtration function.

[Claim 15] An exhaust emission control device given in any one term of claims 10-14 to which the filter with a catalyst function of the above-mentioned exhaust air downstream is characterized by having a surface filtration function.

[Claim 16] An exhaust emission control device given in any one term of claims 10-15 to which the filter with a catalyst function of the above-mentioned exhaust air upstream is characterized by changing using the textile fabrics and/or the nonwoven fabric of ceramic fiber.

[Claim 17] An exhaust emission control device given in any one term of claims 10-16 to which the filter with a catalyst function of the above-mentioned exhaust air downstream is characterized by changing using a ceramic sintered compact.

[Claim 18] An exhaust emission control device given in any one term of claims 10-17 characterized by arranging in the exhaust air upstream of the above-mentioned filter with a catalyst function the HC-SOF removal ingredient which has the function to remove a hydrocarbon and a fusibility organic component, and growing into it.

[Claim 19] The exhaust emission control device according to claim 18 characterized by being at least one sort of zeolites and/or the silica content inorganic substance which were chosen from the silica whose above-mentioned HC-SOF removal ingredients are mordenite, MFI, and beta mold zeolite, and whose average pore diameter is 1-5nm, and the group which consists of a stratified clay mineral.

[Claim 20] The manufacture approach of the exhaust emission control device characterized by making the above-mentioned noble-metals component support with the sinking-in method and/or plating after being the approach of manufacturing the exhaust emission control device of a publication in any one term of claims 7-19 and making the pore wall of the above-mentioned monolith type filter carry out distributed support of the above-mentioned oxide particle.

[Claim 21] When it is the approach of purifying the party curate particle and nitrogen oxides under exhaust air and the temperature of the exhaust air discharged by the internal combustion engine is 500 degrees C or less, they are the following reaction formula 3 and/or 4 $C+H_2O \rightarrow H_2+CO$. -- (3) $C+2H_2O \rightarrow 2H_2+CO_2$ -- (4)

The exhaust air purification approach characterized by including the process in which come out and the hydrogen generation reaction expressed is performed.

[Claim 22] The powder of a porosity particle with which it is an exhaust air purification catalyst including the hydrogen generation catalyst and nitrogen-oxides purification catalyst which are used for the exhaust air purification approach according to claim 21, and the above-mentioned hydrogen generation catalyst supported the rhodium at least, These metals are exhaust air purification catalysts characterized by being contained by the ratio of 0.1-10 when a rhodium is set to 1 including at least one sort of metals chosen from the group which consists of iron, cobalt, manganese, and nickel.

[Claim 23] The exhaust air purification catalyst according to claim 22 to which mean particle diameter of the above-mentioned porosity particle is characterized by being 0.1-20 micrometers.

[Claim 24] The exhaust emission control device characterized by being equipment which purifies the party curate particle and nitrogen oxides under exhaust air using an exhaust air purification catalyst according to claim 22 or 23, arranging the above-mentioned hydrogen generation catalyst in the upstream of an internal combustion engine's exhaust air gas duct, arranging the above-mentioned nitrogen-oxides purification catalyst in the downstream, and changing.

[Claim 25] The exhaust emission control device characterized by being equipment which purifies the party curate particle and nitrogen oxides under exhaust air using an exhaust air purification catalyst according to claim 22 or 23, arranging the layered product of the above-mentioned nitrogen-oxides purification catalyst on an internal combustion engine's exhaust air gas duct, covering the above-mentioned hydrogen generation catalyst and changing on it.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the exhaust air purification approach, an exhaust air purification catalyst, and an exhaust emission control device, and relates to the exhaust air purification approach, exhaust air purification catalyst, and exhaust emission control device which are efficient and can purify the particulate (PM) particle and nitrogen oxides (NO_x) under exhaust air generated from an internal combustion engine etc. in a detail further.

[0002]

[Description of the Prior Art] In recent years, the lean burn engine operated also with an air-fuel ratio higher than theoretical air fuel ratio from a viewpoint of the improvement in fuel consumption and reduction of carbon-dioxide emissions is spreading. Especially the diesel power plant attracts attention anew from because of that of the low fuel consumption.

[0003] However, during exhaust air, including PM which is a part for a solid particulate, since the exhaust-gas temperature is low, with the catalyst of a conventional type, efficient exhaust air purification is in a difficult situation. the engine improvement technique in fuel consumption is markedly alike, and progresses these days, since an exhaust-gas temperature is in the inclination to fall further, purification of exhaust air has become increasingly difficult and the effective approach of carrying out efficient purification of the injurious ingredient under exhaust air of a diesel power plant is desired. Although the oxidation catalyst which comes to support platinum (Pt) into fireproof quantity surface area inorganic support ingredients, such as an alumina (aluminum 2O₃), is used as a catalyst for exhaust air purification of the conventional diesel power plant, oxidation of CO and HC is the main function, and although a certain extent can oxidize, effect is not shown in purification of the dry soot (C= carbon particle) which is the principal component of PM by the amount of SOF, either.

[0004] In order to purify the exhaust air which contains a part for PM like exhaust air of a diesel power plant, a filter technique is indispensable and many the porosity sintered compacts and the fibrous filters which consist of cordierite or silicon carbide are proposed. In addition, as a material of the above-mentioned fibrous filter, what consists of various ingredients, such as an alumina and a silica, is proposed. Moreover, Society of Automotive Engineers of Japan Before [an academic lecture meeting] ** collection Although the diesel particulate filter (DPF) which used silicon carbide fiber is proposed by No.103-98 (1998 autumn conventions), the heater for removing PM which carried out the trap and reproducing a filter is indispensable, and since the complicated system is required, application is difficult for a passenger car with few loading tooth spaces.

[0005] Moreover, NO under exhaust air is converted into NO₂ with strong oxidizing power by arranging Pt system catalyst in the preceding paragraph of a filter as an approach of reproducing a filter without using a heater. This oxidizing power of NO₂ is used. A part for PM which carried out the trap to the filter The approach of burning is proposed (). [JP,1-318715,A, J.P.Warren, et.al.,] ["Effects - after-treatment on particulate matter] when using the Continuously Regenerating Trap", ImechE 1998 S491/006, B.Carberry, et.al., "A focus on current and future particle after-treatment systems", ImechE 1998 S491/007. This approach is a thing using the reaction of the components under exhaust air, and since the combustion purification of the part for PM which carried out the trap can be carried out continuously, it is called the continuation trap oxidizer. However, since the carbon

in PM (C) is a solid particulate, the rate of reaction of NO₂ is comparatively slow, and in order to burn C discharged from the engine at sufficient rate, it is necessary that the conditions of exhaust air require comparatively high temperature conditions 400 degrees C or more, and to increase NO₂ amount from which it becomes an oxidizer in still such a temperature region. That is, in order to purify NO_x which was necessary to increase the NO_x discharge from an engine, consequently increased, the NO_x catalyst of high performance is needed.

[0006] The various approaches for purifying PM and NO_x to coincidence are also proposed. For example, by the emission-gas-purification material which comes to support the catalyst which has a perovskite structure in a porosity filter being proposed by JP,7-116519,A, this makes the particle-like matter and/or hydrocarbon which are contained in exhaust gas act as a reducing agent, it is the approach of returning the nitrogen oxides under exhaust air, this catalyst is used, and they are the following reaction formulae 5 and 6. $C+2NO \rightarrow N_2+CO_2$ -- (5)

$4HC+10NO \rightarrow 5N_2+4CO_2+2H_2O$ -- (6)

It is supposed that it comes out and NO_x is returned by the reaction expressed. In the above-mentioned reaction, since a reaction formula 6 is the reaction of gas molecules, it is difficult for expecting a catalysis to a catalysis being expected, since a reaction formula 5 is the reaction of a solid-state and a gas, and it is unknown whether filter playback can be performed under the usual transit mode conditions.

[0007] On the other hand, arranging an NO_x absorbent and a filter in the location in which heat transfer is possible, and burning PM after NO_x emission reduction from an NO_x absorbent is proposed by the patent printing No. 2722987 official report. Moreover, an NO_x absorbent is supported inside the septum pore of the Wall flow mold filter, and the catalyst which unified the filter and the NO_x absorbent is proposed by JP,9-94434,A.

[0008] These are techniques acquired combining the catalyst and filter which process NO_x, and need respectively different engine control for NO_x processing and PM combustion. In order to use an NO_x absorbent, to absorb NO_x and to return, the control which changes the air-fuel ratio (A/F) of exhaust air is required. Moreover, it is required for combustion of the deposition PM for reproducing a filter, and removal of a sulfur compound by which the trap was carried out to the NO_x absorbent to perform playback of a filter on oxidizing atmosphere conditions to carrying out the temperature up of an NO_x absorbent and/or the filter even more than 600 degrees C or it, and performing removal of the sulfur compound from an NO_x absorbent under reducing atmosphere further. Furthermore, degradation of a catalyst is promoted by elevated-temperature-ization and there is a trouble of forming high cost also systematically again. Control of such an exhaust-gas temperature or an ambient atmosphere (A/F) is complicated, and it is continuously anxious for the exhaust air purification approach in which self-consecration is possible from being accompanied by the sacrifice of fuel consumption or operability, without adding specific control under the usual transit conditions. Moreover, although the proposal which supports a catalyst in a filter was made for the purpose of coincidence removal of PM and NO_x, the device from a viewpoint of contact or the probability of collision of a catalyst component and PM particle had not got used.

[0009] This invention has the place which it is made in view of the technical problem which ***** has such conventionally, and is made into the purpose in offering the exhaust air purification approach which can carry out self-consecration of NO_x and the PM continuously under the usual combustion conditions, without needing specific control, an exhaust air purification catalyst, and an exhaust emission control device.

[0010]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the above-mentioned technical problem being solvable once changing C solid particulate in PM (party curate particle) into a hydrocarbon or hydrogen, and by raising the rate of contact (collision) of a catalyst component and PM particle, and promoting this conversion reaction, as a result of repeating examination wholeheartedly that the above-mentioned technical problem should be solved.

[0011] Namely, the exhaust air purification approach of this invention is the approach of purifying the party curate particle and nitrogen oxides under exhaust air, and is the following reaction formula 1. $mC+nH_2O \rightarrow H_2nCm+n/2O_2$ -- (1)

It is characterized by including the process in which come out and a party curate particle is changed into a hydrocarbon by the reaction expressed.

[0012] Moreover, the above-mentioned hydrocarbon is made to react with nitrogen oxides, and the suitable gestalt of the exhaust air purification approach of this invention is the following reaction formula 2. $H_2nCm + 4NO \rightarrow 2N_2 + mCO_2 + nH_2O$ -- (2)

It is characterized by including the process out of which it comes and which is changed into nitrogen, a carbon dioxide, and water by the reaction expressed.

[0013] Furthermore, the exhaust emission control device of this invention is equipment which purifies the party curate particle and nitrogen oxides under exhaust air using the above-mentioned exhaust air purification approach. At least one sort of noble-metals components chosen from the group which changes from platinum, palladium, and a rhodium to the pore wall of a monolith type filter, It is characterized by arranging in an internal combustion engine's exhaust air gas duct the filter with a catalyst function with which a mean diameter supports at least one sort of oxide particles chosen from the group which consists of the alumina which is 1 micrometer or less, a titania, a zirconia, and a silica, and changes.

[0014] Furthermore, the porosity of the above-mentioned monolith type filter is 30 - 80%, and the suitable gestalt of the exhaust emission control device of this invention is characterized by an average pore diameter being 5-40 micrometers again.

[0015] Moreover, other suitable gestalten of the exhaust emission control device of this invention are characterized by dividing the above-mentioned filter with a catalyst function into two or more steps, arranging it at a serial, and changing.

[0016] Furthermore, the suitable gestalt of further others of the exhaust emission control device of this invention is characterized by arranging in the exhaust air upstream of the above-mentioned filter with a catalyst function the HC-SOF removal ingredient which has the function to remove a hydrocarbon and a fusibility organic component, and growing into it.

[0017] Furthermore, the manufacture approach of the exhaust emission control device of this invention is an approach of manufacturing the above-mentioned exhaust emission control device, and after making the pore wall of the above-mentioned monolith type filter carry out distributed support of the above-mentioned oxide particle, it is characterized by making the above-mentioned noble-metals component support with the sinking-in method and/or plating again.

[0018] Moreover, other exhaust air purification approaches of this invention are the following reaction formula 3 and/or 4 $C + H_2O \rightarrow H_2 + CO$, when it is the approach of purifying the party curate particle and nitrogen oxides under exhaust air and the temperature of the exhaust air discharged by the internal combustion engine is 500 degrees C or less. -- (3)

$C + 2H_2O \rightarrow 2H_2 + CO_2$ -- (4)

It is characterized by including the process in which come out and the hydrogen generation reaction expressed is performed.

[0019] Furthermore, the powder of a porosity particle with which the exhaust air purification catalyst of this invention is an exhaust air purification catalyst including the hydrogen generation catalyst and nitrogen-oxides purification catalyst which are used for the above-mentioned exhaust air purification approach, and the above-mentioned hydrogen generation catalyst supported the rhodium at least, It is characterized by containing these metals by the ratio of 0.1-10 including at least one sort of metals chosen from the group which consists of iron, cobalt, manganese, and nickel, when a rhodium is set to 1.

[0020] Furthermore, other exhaust emission control devices of this invention are equipment which purifies the party curate particle and nitrogen oxides under exhaust air using the above-mentioned exhaust air purification catalyst, and are characterized by arranging the above-mentioned hydrogen generation catalyst in the upstream of an internal combustion engine's exhaust air gas duct, arranging the above-mentioned nitrogen-oxides purification catalyst in the downstream, and changing again.

[0021] Moreover, the exhaust emission control device of further others of this invention is equipment which purifies the party curate particle and nitrogen oxides under exhaust air using the above-mentioned exhaust air purification catalyst, arranges the layered product of the above-mentioned nitrogen-oxides purification catalyst on an internal combustion engine's exhaust air gas duct, and is characterized by covering the above-mentioned hydrogen generation catalyst and

changing on it.

[0022]

[Embodiment of the Invention] Hereafter, the exhaust air purification approach of this invention is explained to a detail. In addition, mass percentage is shown unless it mentions specially "%" in this specification.

[0023] The exhaust air purification approach of this invention is the approach of purifying the particulate (PM) particle and nitrogen oxides (NO_x) under exhaust air, and is characterized by being efficient and purifying PM particle under exhaust air which cannot burn easily on the usual transit conditions by changing PM particle into a hydrocarbon (HC). Moreover, NO_x is changed into harmless nitrogen (N₂), CO₂, and H₂O by making it react with NO_x while exhausting generated HC. In addition, generated HC may oxidize immediately and may be changed into a carbon dioxide (CO₂) or water (H₂O).

[0024] That is, with the exhaust air purification approach of this invention, they are the following reaction formulae 1 and 2. $mC+nH_2O \rightarrow H_2nCm+n/2, O_2$ -- (1)

$H_2nCm+4NO \rightarrow 2N_2+mCO_2+nH_2O$ -- (2)

NO_x and PM are mostly removed by coincidence by coming out and advancing the conversion reaction expressed. Although the detail of the mechanism from which C in PM is changed into HC in HC generation reaction (formula 1) by C and H₂O here was unknown at present, this invention persons performed evaluation to which for example, Pt / alumina system catalyst were made to react with the model gas of C (graphite)/O₂-/H₂ O/N₂ system, and as shown in the graph of drawing 1, they detected HC. Moreover, as it evaluated by carrying out additional installation of the NO into model gas and was shown in drawing 2, it checked that NO concentration decreased. Therefore, it can guess that HC generation reaction (formula 1) and the HC-NO reaction (formula 2) have occurred.

[0025] Furthermore, in order to advance the above-mentioned HC generation reaction (formula 1) and a HC-NO reaction (formula 2), it is desirable to make temperature conditions into 350 degrees C or less, and it is more desirable to consider especially as 280 degrees C or less so that the graph of drawing 1 which is an example, and drawing 2 may also show. In addition, although minimum temperature changes with engine performance of a catalyst etc., if it is 200 degrees C or more in temperature in general, a remarkable reaction rate will be obtained. Here, on temperature conditions higher than 350 degrees C, it is thought that oxidation reaction of HC generated at the above-mentioned HC generation reaction (formula 1) becomes superior, and the above-mentioned HC-NO reaction (formula 2) also becomes inferior in strength. On the other hand, it is known that the HC-NO_x reaction (formula 2) on Pt system catalyst in exhaust air conditions with much oxygen (lean burn engine etc.) will advance notably in general in a 150 degrees C - 300 degrees C temperature region. Thus, if the exhaust air purification approach of this invention is used, since the above-mentioned HC generation reaction (formula 1) and a HC-NO reaction (formula 2) may be comparatively advanced by the low temperature service, without performing specific engine control, PM is efficient and can purify the exhaust air from the diesel power plant which poses a serious problem.

[0026] Next, the exhaust emission control device of this invention is explained to a detail. Although it was an indispensable condition to use a catalyst in order to have advanced above-mentioned HC generation reaction (formula 1) and the above-mentioned above-mentioned HC-NO reaction (formula 2), this invention persons did the knowledge of it being very effective that a catalyst and PM particle contact directly at this reaction. For example, the above-mentioned HC generation reaction (formula 1) advances, only when Pt / alumina system catalyst powder, and carbon (C) powder are mixed well enough, and when mixing is inadequate, it does not advance. The exhaust emission control device of this invention uses a filtration function positively as a means which raises the contact (collision) probability of a catalyst component and PM particle from this viewpoint. That is, it considers as the exhaust emission control device which has a filtration function and a catalyst function, and the contact (collision) probability of the PM particle and the catalyst component which flow in narrow pore by making a catalyst component distribute and support on the pore wall front face of a filter is raised. In addition, as the support approach of the above-mentioned catalyst component, the support approach which covers the wall whole surface with plating etc. is effective

so that it may mention later.

[0027] Here, the exhaust emission control device of this invention makes the pore wall of a monolith type filter support platinum (Pt), palladium (Pd) or (Rh), and the noble-metals component that consists of the combination of such arbitration as the above-mentioned catalyst component, and, specifically, grows into it. When it is not necessary to use especially a noble-metals component independently and is used combining two or more components at this time, the above-mentioned HC generation reaction (formula 1) and a HC-NO reaction (formula 2) can be advanced more smoothly. For example, in the combination of Pt and Rh, HC generation reaction (formula 1) can be promoted by Pt, and a HC-NO reaction (formula 2) can be promoted by Rh.

[0028] Moreover, the pore wall of the above-mentioned monolith type filter is made to support the oxide particle by which mean particle diameter is specifically applied to the oxide particle of fines 1 micrometer or less, the alumina (aluminum $2O_3$) used from the former as support of a noble-metals component, a titania (TiO_2), a zirconia (ZrO_2) or a silica (SiO_2), and the combination of such arbitration. From this, pore is not blockaded but a catalyst component distributes good on the front face of a pore wall. Furthermore, as for the above-mentioned mean particle diameter, it is more desirable that it is 0.6 micrometers or less. Furthermore, even if the above-mentioned oxide particle is independent, it can be used, but when supporting two or more sorts of catalyst components and it is used combining two or more sorts of oxide particles, there is a more effective thing again. In addition, if mean particle diameter exceeds 1 micrometer, the pore of the above-mentioned monolith type filter may be blockaded. Moreover, the above-mentioned oxide particle can make the water solution of the hydroxide which can generate this oxide particle, or a nitrate able to permeate the pore wall of a filter, and it can carry out distributed support.

[0029] Furthermore, as the support approach of the above-mentioned noble-metals component or an oxide particle, a filter pore wall is made to carry out osmosis support of the powder of an oxide particle, and the approach of subsequently making a noble-metals component supporting, the method of making a filter pore wall carry out immersion support of this oxide particle, after making an oxide particle support a noble-metals component beforehand, etc. can be illustrated. The former is more effective in order to expose a noble-metals component to a particle front-face side as much as possible especially.

[0030] Furthermore, as support of the above-mentioned noble-metals component or an oxide particle, the filter of the monolith type which has a filtration function is used again. As for this monolith type filter, at this time, it is desirable for the basic property as a filter to be excellent, i.e., for them to be high collection efficiency, the amount of quantity uptake, and low voltage loss. Moreover, it is good to be able to support a catalyst component (noble-metals component) on a pore wall front face, and to make it contact by PM particle whose catalyst component of this is under exhaust air, and the high probability.

[0031] Moreover, in the above-mentioned monolith type filter, it is suitable for porosity that it is 30 - 80%. When porosity is less than 30%, the large filter size for filling the predetermined engine performance must be taken, and loading nature may get worse. Moreover, when it exceeds 80%, reinforcement may fall and loading nature may get worse. Furthermore, it is suitable for a pore diameter that it is 5-40 micrometers in an average pore diameter. At this time, it is suitable for the particle size of the catalyst component which the magnitude of pore supports, and since invasion of PM particle is attained easily and it can increase a contact probability with a cell wall, it is effective. If smaller than 5 micrometers, even if invasion of PM particle will become difficult and it will invade, it may be hard to move in the inside of pore. On the other hand, when larger than 40 micrometers, the contact probability of PM particle and a cell wall will fall, and will pass through the inside of pore, without reacting.

[0032] Furthermore, as the above-mentioned monolith type filter, ceramic sintered compacts, such as cordierite, a mullite, and SiC , textile fabrics, a nonwoven fabric of ceramic fiber (fiber), etc. can be used again. Moreover, if a filter configuration is for example, the above-mentioned ceramic sintered compact and they are a honeycomb mutual weather-strip type, and textile fabrics and the nonwoven fabric of the above-mentioned ceramic fiber, it can mention what wound around a certain base material, or was fabricated in the request configuration. In addition, although especially the above-mentioned monolith type filter is not limited, using properly according to each property is important

for it. For example, although the filter which consists of a fiber is disadvantageous to raise collection efficiency, it is easy to be able to make pore diameter distribution large comparatively and to apply it to exhaust air of broad PM particle diameter. Since especially the fiber is comparatively flexible, its contact probability with PM particle is high, and is effective in processing of big PM particle which cannot react more easily. Moreover, when carrying out division arrangement of the filter in two or more steps, it is good to arrange the filter which used the textile fabrics and/or the nonwoven fabric of ceramic fiber for the exhaust air upstream, and it good to arrange the honeycomb mold filter which used the ceramic sintered compact for the exhaust air downstream. In addition, since a touch area can take a large honeycomb mold filter also in small size comparatively, it is a typical filter of amount of low voltage loss-quantity uptake-quantity collection efficiency.

[0033] Moreover, it is suitable for the filter with a catalyst function which made the above-mentioned monolith type filter support a catalyst component to divide into two or more steps and to arrange. In this case, since the filter with a catalyst function with which the exhaust air upstream and the downstream are different in a property can be arranged, it is effective. For example, as shown in drawing 4, the above-mentioned filter with a catalyst function can be divided into two steps, and it can arrange to a serial. From this, the pore passage distance of PM particle can be earned, and since the count of a collision of PM particle to the filter pore wall with which the catalyst component was supported increases, the effectiveness of the above-mentioned HC generation reaction (formula 1) or the above-mentioned HC-NO reaction (formula 2) may improve sharply.

[0034] Furthermore, it is suitable to make pressure loss of the filter of the exhaust air upstream larger than the pressure loss of the filter of the exhaust air downstream with the filter with a catalyst function which carried out [above-mentioned] division arrangement. Usually, although division arrangement will raise pressure loss, that effect can be suppressed in this case. If this is important also when raising the contact probability of PM particle and a catalyst component, and it catches most PM particles with the filter of the upstream, it becomes more superior [the rate of sedimentation] than a reaction rate, and a filter tends to blockade it. In addition, the pressure loss of a filter can change and control porosity, an average pore diameter, etc. of a filter. Consequently, PM collection efficiency can also be changed.

[0035] Furthermore, it is desirable to arrange a filter with comparatively low collection efficiency to the exhaust air upstream, and to arrange a filter with high collection efficiency from the field of PM collection efficiency, to the exhaust air downstream again. In other words, it is good to make the average pore diameter and porosity of a filter of the exhaust air upstream larger than the average pore diameter and porosity of a filter of the exhaust air downstream. In this case, the rate of a deployment of C particle to HC generation is raised, and the rate of NO_x purification may improve.

[0036] Although PM particle of a comparatively big particle size is caught by the filter of the exhaust air upstream at this time, whenever it contacts a catalyst component within a filter, a particle front face is changed into HC, and it moves in the inside of pore, reducing particle size. However, when there is a part in which a catalyst component does not exist within a filter, it is fixed there and PM particle may serve as a nucleus of lock out. For this reason, its PM collection efficiency is low rather, the filter installed in the exhaust air upstream has the effective type which cannot cause lock out easily, and it is desirable that it is the filter which has the so-called structure of a collision filtration method. For example, a form mold, a fiber mold, etc. which have a three-dimension mesh random structure are mentioned. Since PM particle by which the part where, especially as for the filter of the above-mentioned fiber mold, the coat of the catalyst component was carried out was flexibly caught between fibers since it was able to expand and contract is movable, pushing away a fiber particle by exhaust gas pressure, it is hard to blockade filter pore and the contact probability of a catalyst component and PM particle can be earned, a reaction is easy to be promoted. On the other hand, it is suitable for the exhaust air downstream to arrange the filter of high collection efficiency, the amount of high uptake, and low voltage loss. It is because carried out the extent reaction and low size is formed, so the property which is the upstream of catching certainly and making it reacting completely is required for PM particle of the exhaust air downstream. For example, the filter which has a surface filtration function can be used.

[0037] Moreover, although HC and SOF which are contained during exhaust air can raise purification effectiveness by strengthening an adsorption function and an oxidation function using a

catalyst, if even a filter reaches, they may react with NO_x on the catalyst component of a pore wall, or they may cover a pore wall, i.e., a catalyst front face, and may do a bad influence, such as barring a catalysis. Then, the amount of [HC or] SOF is effective when promoting the alternative reaction of HC and NO_x which carry out the trap in the upstream of a filter beforehand and which were generated from C within the filter demonstrates an exhaust air cleaning effect. It is desirable to specifically arrange in the exhaust air upstream of a filter the HC-SOF removal ingredient which has the function to remove a hydrocarbon and a fusibility organic component. this -- 350 degrees C or less -- efficient purification of PM and NO_x is comparatively attained also on low emission temperature conditions. A HC-SOF removal ingredient can be arranged as shown in drawing 3 or drawing 4 . Moreover, as a HC-SOF removal ingredient, mordenite, MFI, beta mold zeolite, and an average pole diameter can use suitably the silica which is 1-5nm or a stratified clay mineral and the zeolite concerning the combination of such arbitration, and/or a silica content inorganic substance. In addition, as the above-mentioned silica, the porous body of the oxide called the so-called meso porous silica is mentioned, for example, it can obtain, using a surfactant as mold. When the average pole diameter of a pole diameter is too small in less than 1nm, and sufficient adsorption prehension for HC and SOF cannot be performed but it exceeds 5nm, a pole diameter is too large and HC and the adsorption effectiveness for SOF may fall. Moreover, hectorite, a montmorillonite, etc. are mentioned as the above-mentioned stratified clay mineral. It becomes possible for them, while these porous body ingredients are efficient and carry out adsorption prehension of HC or the SOF by the upstream of a filter to oxidation remove [which used gaseous-phase oxygen by adding catalyst components, such as Pt and Pd, further], and the rate of a deployment of the generation HC in a filter pore wall is raised. The above-mentioned porous body ingredient can be coated and used for the honeycomb support made from the so-called flow through type which has about 400 holes per 1 square inch of cordierite. In order to coat a honeycomb object with the powder of this porous body and to make a honeycomb side pasted up and fixed, it is common to use sintering agents (binder), such as alumina sol and a silica sol. Moreover, oxidation removal of HC which stuck to the porous body ingredient, or SOF can be promoted by adding catalyst components, such as Pt and Pd. In this case, the powder which could make this porous body ingredient support a direct catalyst component, and made support, such as an alumina and a titania, support a catalyst component beforehand may be mixed and used for porous ingredient powder.

[0038] After making the pore wall of the above-mentioned monolith type filter carry out distributed support of the above-mentioned oxide particle, the exhaust emission control device mentioned above makes the above-mentioned noble-metals component support with the sinking-in method and/or plating, and is obtained. In addition, the sinking-in method regularly used with the usual catalyst method of preparation is effective, and it is [it is more effective to use plating which can cover a filter pore wall, and] also effective to use plating and the sinking-in method together further. As plating, various kinds of approaches are effective and can apply suitably an electrolytic decomposition process, a non-electrolytic decomposition process, etc. typically.

[0039] As mentioned above, the exhaust air A/F fluctuation control for removing the various exhaust air temperature up control for burning PM deposited on the filter, and NO_x, and since an NO_x adsorption function is not used further, the exhaust emission control device of this invention does not need specific control of S desorption control from an NO_x adsorption catalyst etc., but can control aggravation of fuel consumption. Moreover, since C can be purified at low temperature, there is no fear of breakage by the heat of a filter, and it can be equal to prolonged use. For example, in a diesel power plant, clean exhaust air can be realized and the automobiles excellent in economical efficiency (fuel consumption) with little environmental pollution including the problem of global warming can be offered.

[0040] Next, other exhaust air purification approaches, exhaust air purification catalysts, and exhaust emission control devices of this invention are explained to a detail. This exhaust air purification approach generates hydrogen from the soot (PM particle) adhering to a catalyst, and purifies NO_x using the hydrogen. That is, when the temperature of the exhaust air discharged by the internal combustion engine is 500 degrees C or less, they are the following reaction formula 3 and/or 4 C+H₂O->H₂+CO. -- (3)
C+2H₂O->2H₂+CO₂ -- (4)

It comes out and the hydrogen generation reaction expressed is performed. From this, hydrogen is generated from PM particle and even the temperature of 500 degrees C or less can purify NOx using this hydrogen.

[0041] Here, as a reducing agent of NOx, HC under exhaust air, CO, and when using H2 further, since oxygen exists mostly in lean atmosphere, these reducing agents will usually be set to H2O or CO2. Therefore, when lean atmosphere purified exhaust air (lean burn engine etc.) of most service conditions, there was fault that the above-mentioned hydrogen generation reaction (formulas 3 and 4) could not use effectively. Moreover, in the lean atmosphere of hyperoxia, PM adhering to a catalyst hardly performs a steam and a hydrogen generation reaction (formulas 3 and 4).

[0042] PM which exists during exhaust air richly [the exhaust air purification catalyst of this invention] regardless of Lean's ambient atmosphere is made to adhere to a catalyst front face. And not only a rich ambient atmosphere but lean atmosphere is mainly used for a hydrogen generation reaction (formulas 3 and 4) according to an operation of Rh, and hydrogen generates this PM. Therefore, NOx can be returned from the hydrogen which also generated lean atmosphere, and the NOx purification engine performance can be improved. Moreover, since SOx of the NOx adsorption site by which sulfur poisoning was carried out can also be returned by hydrogen, while NOx adsorption capacity is recoverable, new sulfur poisoning can be prevented. The NOx purification engine performance can be improved also by this.

[0043] What specifically contains the powder of the porosity particle which supported the rhodium (Rh) at least, and iron (Fe), cobalt (Co), manganese (Mn) or nickel (nickel) and the metal concerning the combination of such arbitration as the above-mentioned H2 generation catalyst is used. At this time, metals, such as Above Fe, Co, Mn, and nickel, are good to be supported by the above-mentioned porosity particle. By using this H2 generation catalyst, the high NOx purification engine performance can be discovered by H2 made to generate from PM and H2O at the temperature of 500 degrees C or less. Moreover, since the reactivity of PM, and H2 and NOx which were generated from H2O will improve in order to adsorb NOx by Lean if NOx adsorption material is used further so that it may mention later, the purification reaction of NOx can be promoted. Furthermore, when SOx under exhaust air reacts with an NOx adsorption site and forms SOx adsorption species and a SOx salt in a catalyst front face, NOx adsorption capacity may disappear (the so-called sulfur poisoning), but since SOx is returned by the above-mentioned H2 which carried out generation, sulfur poisoning can be prevented. Furthermore, it is returned by H2 and NOx adsorption capacity also tends to revitalize the NOx adsorption site which received sulfur poisoning again.

[0044] Moreover, when metals, such as Above Fe, Co, Mn, and nickel, set Rh to 1, they are contained in the above-mentioned H2 generation catalyst by the ratio of 0.1-10. It is more desirable that it is especially 1-5. If smaller than 0.1, the effectiveness by these metals will not show up and it will not be different from the case of only Rh. On the other hand, if 10 is exceeded, the activity of Rh will fall, and the reactivity of PM and Rh will get worse. Furthermore, as for Above Rh, it is desirable to be supported in the per [120g of porosity particles / 0.05-20g] range. If there are few amounts of support of Rh than 0.05g/120g, endurance will tend to fall, and if [than 20g/120g] more, while the above-mentioned effectiveness will be saturated, it is easy to cause increase of cost.

Furthermore, platinum (Pt), palladium (Pd), iridium (Ir), etc. can also be supported with Rh, and the amount of support at this time should just make the sum total of Rh and these metals the above-mentioned range. In addition, as for Pt supported by the above-mentioned porosity particle, it is desirable that it is the range of per [0.1-10g] 120g of porosity particles. If there are few amounts of support of Pt than 0.1g/120g, the rate of purification of HC, CO, and NOx will tend to fall, and even if [than 10g/120g] more, while effectiveness is saturated, it is easy to cause increase of cost.

[0045] Moreover, as the above-mentioned porosity particle, it can choose from an alumina, a silica, a titania, a zirconia, a silica alumina, a zeolite, etc. suitably, and one sort can be used independently or two or more classes can be used, for example, mixing or compound-izing. However, as for Zr with bad thermal resistance, it is desirable to use an alumina, zirconia, or zirconia-alumina for Rh support powder from reasons congenial to Rh. Furthermore, as for the particle size of the above-mentioned porosity particle, it is desirable that it is the range of 0.1-20 micrometers. If larger than 20 micrometers, the probability for Rh powder to approach will become high, degree of dispersion of Rh falls [if particle size is smaller than 0.1 micrometers, degree of dispersion of Rh will fall, / the

H₂ generation effectiveness from PM and H₂O is fully hard to be acquired] as a result, and the H₂ generation effectiveness by PM and H₂O may not fully be acquired.

[0046] In addition, the above-mentioned porosity particle can also be made to support NO_x adsorption material further, and NO_x adsorption capacity can be improved further in this case. As this NO_x adsorbent, alkali metal, alkaline earth metal or a rare earth metal, the metal concerning the combination of such arbitration, etc. can be used. Specifically as an alkali metal, a lithium (Li), sodium (Na), a potassium (K), caesium (Cs), etc. are mentioned. As an alkaline earth metal, the magnesium (Mg) which is a periodic table 2A group element, calcium (calcium), strontium (Sr), barium (Ba), etc. are mentioned. As a rare earth metal, a lanthanum (La), a cerium (Ce), a praseodymium (Pr), etc. are mentioned. Moreover, as for this NO_x adsorption material, it is desirable to make it support in 0.05-3.0 mols per 120g of porosity particles. Effectiveness tends to be saturated, even if the rate of NO_x purification will tend to fall and it will support mostly from 3.0 mols / 120g, if there are few amounts of support than 0.05 mols / 120g. Furthermore, when the above-mentioned porosity particle is made to support Rh and Pt, it is good to manufacture separately Rh support porosity particle (the 1st powder) and Pt support porosity particle (the 2nd powder), and to mix these with Rh after that, in order to pull out an operation of metals, such as nickel, Fe, Co, and Mn, etc. enough. in this case, the mixing ratio of the 1st powder and the 2nd powder -- weight ratio conversion of Rh and Pt -- 1st powder: -- the 2nd -- the range of powder = 0.05:1-1:1 is desirable. moreover, the case where both the 1st powder and the 2nd powder use an alumina as a porosity particle -- weight ratio conversion of an alumina -- 1st powder: -- the 2nd -- the range of powder = 0.1:1-2:1 is desirable. If it separates from these range, the case of the excess and deficiency of above-mentioned Rh and above-mentioned Pt and the same fault may occur. Moreover, when the above-mentioned porosity particle is made to support transition metals, it is desirable to make Mg support further. By using this co-catalyst, since a hydrogen generation reaction is easy to be promoted, it is effective.

[0047] In this invention, it can consider as the exhaust emission control device which purifies the party curate particle and nitrogen oxides under exhaust air using an above-mentioned exhaust air purification catalyst. That is, the exhaust emission control device of this invention arranges the above-mentioned hydrogen generation catalyst in the upstream of an internal combustion engine's exhaust air gas duct, arranges the above-mentioned nitrogen-oxides purification catalyst in the downstream, and grows into it. By considering as such a configuration, it becomes the exhaust emission control device which promotes the above-mentioned hydrogen generation reaction (formulas 3 and 4). Moreover, other exhaust emission control devices of this invention arrange the layered product of the above-mentioned nitrogen-oxides purification catalyst on an internal combustion engine's exhaust air gas duct, on it, cover the above-mentioned hydrogen generation catalyst, and change. For example, an NO_x catalyst can be multilayered and Rh powder containing the metal which changes from Fe, Co, Mn or nickel, and the combination of such arbitration to the maximum upper layer can be covered.

[0048]

[Example] Hereafter, although an example and the example of a comparison explain this invention to a detail further, this invention is not limited to these examples.

[0049] In the following examples 1-3 and examples 1-3 of a comparison, the performance evaluation test was performed about the exhaust emission control device of this invention, i.e., the exhaust emission control device which used (Hydrocarbon HC) generation catalyst.

[0050] (Example 1) After dipping honeycomb mold mutual weather-strip filter made from cordierite 2.5L which is 18 micrometers in 60% of porosity, and average pore diameter, and has the air hole of about 200 cels per 1 square inch in the nitric-acid aqueous acids which the water solution of an aluminium nitrate was made to distribute a super-particle alumina with a mean particle diameter of 0.5 micrometers, and were obtained, the hot-air-drying-baking process was repeated 3 times and the pore wall of a filter was made to carry out distributed support of the alumina. The amount of support of the alumina at this time was 85g of filter volume 1L per abbreviation. Moreover, this filter was dipped in the dinitrodiammine Pt water solution whose Pt concentration is about 2.5%, the hot-air-drying-baking process was repeated twice, and the alumina made [the pore wall of a filter] to carry out distributed support was made to support Pt. Furthermore, electroless deposition was performed to

this filter and filter catalyst 1A was obtained. Plating dipped the above-mentioned honeycomb filter in the plating bath water solution containing Pt and a reducing agent, deposited Pt, and was obtained. The amount of support of Pt at this time was 10g of filter volume 1L per abbreviation.

[0051] The honeycomb-like monolith material (honeycomb catalyst 1B) which has the function which carries out adsorption treatment of HC and SOF which are arranged in the preceding paragraph of this filter catalyst 1A was obtained as follows. Pt / gamma alumina powder which was made to support Pt 2.5% to the activated alumina which uses the gamma alumina of specific-surface-area of about 220m²/g as a principal component, and obtained it to it by the sinking-in method Specific-surface-area about 830m²/g and a porous silica with an average pore diameter of about 3.2nm, By specific-surface-area of 450m²/g, the silica-alumina ratio about 90 zeolite beta Furthermore, the MFI zeolite of the silica-alumina ratio 70 [about] was mixed by the weight ratio 1:4:1 by specific-surface-area of 350m²/g, and it mixed by the weight ratio of 5:6:1 with boehmite powder, and nitric-acid acidity alumina sol was added further 1%, it mixed with water, and slurry liquid was obtained. Cordierite honeycomb 1.5L which has the air hole of 400 cels per 1 square inch was coated with this slurry, it passed through the process of desiccation and baking, and honeycomb catalyst 1B which has the function which adsorbs and decomposes HC and SOF was obtained. The exhaust emission control device 1 was obtained by including in one converter in the preceding paragraph and the latter part, combining respectively the above, honeycomb catalyst 1B, and filter catalyst 1A.

[0052] (Example 2) A honeycomb catalyst was not installed in the preceding paragraph, but except having been referred to only as filter catalyst 2A, the same actuation as an example 1 was repeated, and the exhaust emission control device 2 was obtained.

[0053] Honeycomb mold mutual weather-strip filter made from cordierite 1.25L which is 18 micrometers in 60% of porosity, and average pore diameter, and has the air hole of about 200 cels per 1 square inch, (Example 3) It was 32 micrometers in 65% of porosity, and average pore diameter, and honeycomb mold mutual weather-strip filter made from cordierite 1.25L which has the air hole of about 200 cels per 1 square inch was prepared, the almost same actuation as an example 1 was repeated, and two filter catalysts three A1 and three A2 were obtained. Such filter catalysts three A1 and three A2 and honeycomb catalyst 3B have been arranged to the serial, and the exhaust emission control device 3 was obtained. That is, these catalysts have been arranged from the exhaust air upstream in order of the honeycomb catalyst 3B-filter catalyst 3A2-filter catalyst three A1.

[0054] (Example 1 of a comparison) Pt / gamma alumina powder which was made to support Pt 2.5% to the activated alumina which uses the gamma alumina of specific-surface-area of about 220m²/g as a principal component, and obtained it to it by the sinking-in method were mixed with boehmite powder by the weight ratio of 10:2, and nitric-acid acidity alumina sol was added further 1%, it mixed with water, and slurry liquid was obtained. 100 g/L coating of this slurry was carried out at cordierite honeycomb 1.5L which has the air hole of 400 cels per 1 square inch, and honeycomb-like oxidation catalyst R1B was obtained through the process of desiccation and baking. The exhaust emission control device R1 which becomes the example 1 of a comparison was obtained by arranging to a serial honeycomb mold mutual weather-strip filter made from cordierite 2.5L which has the air hole of about 200 cels per 1 square inch, and including in one converter with this honeycomb-like oxidation catalyst R1B, and the porosity of 60% and the average pore diameter of 18 micrometers. In addition, this equipment R1 has a configuration similar to the so-called conventional continuation trap oxidizer.

[0055] (Example 2 of a comparison) The same honeycomb mold mutual weather-strip filter made from cordierite 2.5L as an example 1 was coated with the slurry of the same Pt/gamma alumina catalyst as the example 1 of a comparison, by repeating a hot-air-drying-baking process 4 times, one side of a filter was made to support Pt/alumina catalyst, and filter catalyst R2A was obtained. The amount of support of Pt/alumina catalyst at this time was 100g of filter volume 1L per abbreviation. Only by this filter catalyst R2A, the exhaust emission control device R2 was obtained. In addition, this exhaust emission control device R2 does not make what changed the process of a filter catalyst, i.e., a filter wall front face, support Pt/alumina catalyst as compared with the exhaust emission control device 2 of an example 2, but forms a catalyst bed in a filter outer wall.

[0056] (Example 3 of a comparison) The exhaust emission control device R3 was obtained by

arranging the honeycomb catalyst 1B same in the preceding paragraph of the same filter catalyst R2A as the example 2 of a comparison as an example 1, and including in one converter.

[0057] The performance evaluation test of the exhaust emission control device of an example and the example of a comparison was performed using the engine DYNAMO equipment which installed the direct injection mold diesel power plant of 4-cylinder 2.5L equipped with the <example of evaluation trial> common rail system. In addition, what can control the exhaust-gas temperature of a catalyst system inlet port by the engine load, an inhalation-of-air diaphragm, and postinjection by the common rail system was used for this evaluation equipment. Moreover, the transient performance-evaluation method which repeats the pattern which the performance-evaluation method of an exhaust emission control device holds the inlet temperature of equipment at 250 degrees C for 2 minutes, subsequently holds it at 300 degrees C for 3 minutes, and is held for 1 minute at 350 more degrees C for 5 hours was used. In addition, Sweden class 1 gas oil was used in this evaluation trial.

[0058] In the above-mentioned evaluation trial, when the rate of average reduction of PM and NOx was computed about the exhaust emission control device 1 (example 1), PM elimination factor was 93% and the NOx elimination factor was 46%. Moreover, the pressure loss rise after 5-hour operation to the first stage was 25mmHg. Similarly, PM elimination factor was [NOx of the rate / in / about an exhaust emission control device 2 (example 2) / operation 2 hours / of reduction] 55% of elimination factors 90%. Moreover, the pressure loss rise after 4-hour operation to the first stage is 32mmHg, covering of the catalyst component by SOF in PM takes place, and it is thought that the oxidation engine performance fell with time. By removing a part for SOF by the preceding paragraph side shows from this that prevent covering of a catalyst and endurance increases like an exhaust emission control device 1. Moreover, about the exhaust emission control device 3 (example 3), PM elimination factor was 95% and the NOx elimination factor was 57%. Moreover, the pressure loss rise after 5-hour operation to the first stage was 18mmHg. This shows that the effectiveness which divided the filter is demonstrated.

[0059] On the other hand, about the exhaust emission control device R1 (example 1 of a comparison), PM elimination factor was 95%, the NOx elimination factor was 2%, the rate of NOx reduction was low compared with the example, and since the pressure loss rise 3 hours after operation exceeded 40mmHg(s) and the engine load became large, operation was canceled at the time. Moreover, since PM elimination factor is 92%, and an NOx elimination factor is 8%, and the pressure loss rise 3 hours [to the first stage] after operation exceeded 40mmHg(s) about the exhaust emission control device R2 (example 2 of a comparison) and the engine load became large, operation was canceled at the time. Furthermore, since PM elimination factor is 92%, and an NOx elimination factor is 11%, and the pressure loss rise after 4-hour operation to the first stage exceeded 40mmHg (s) about the exhaust emission control device R3 (example 3 of a comparison) and the engine load became large, operation was canceled at the time.

[0060] Moreover, when it changes to the pattern which holds inlet temperature at 300 degrees C for 5 minutes, and holds the performance-evaluation conditions of an exhaust emission control device for 2 minutes at 400 more degrees C, as for the rate of average reduction of PM and NOx by the exhaust emission control device 1 after 5-hour operation, it turns out that an NOx elimination factor becomes [PM elimination factor] 16% 91%, and the rate of reduction of NOx gets worse especially on elevated-temperature exhaust air conditions from this. An exhaust-gas temperature uses it on conditions 350 degrees C or less, since effectiveness is large, it is clear that it is suitable for exhaust air purification of an efficient internal combustion engine with a low exhaust-gas temperature, but if the exhaust emission control device of this invention adjusts temperature conditions by choosing an arrangement location suitably etc. also to an internal combustion engine with a high exhaust-gas temperature, correspondence of it will be attained.

[0061] As mentioned above, if the exhaust emission control device of this invention is used, about 200-350 degrees C since it is efficient and exhaust air of low emission temperature conditions can be purified comparatively, even if it does not use the special engine controlling method, clean exhaust air is easily realizable.

[0062] Next, in the following examples 4-9 and examples 4-7 of a comparison, the performance evaluation test was performed about the exhaust air purification catalyst which changes including the exhaust air purification catalyst, i.e., the hydrogen (H₂) generation catalyst, and nitrogen-oxides

(NOx) purification catalyst of this invention.

[0063] (Example 4) It sank into activated-alumina powder (mean particle diameter of 1 micrometer), the nitric-acid Fe water solution was calcinated at 400 degrees C among after [desiccation] air for 1 hour, and Fe support alumina powder (powder 1) was obtained. Fe concentration of this powder was 2%. It sank into powder 1, the nitric-acid Rh water solution was calcinated after desiccation at 400 degrees C of N₂ Naka for 1 hour, and Rh and Fe support alumina powder (powder 2) were obtained. Rh concentration of this powder was 2% (Fe/Rh is a mole ratio and is 0.54). It sank into activated-alumina powder, the JIATORO diamine Pt water solution was calcinated at 400 degrees C among after [desiccation] air for 1 hour, and Pt support alumina powder (powder 3) was obtained. Pt concentration of this powder was 2%.

[0064] 70g and an alumina were fed into 70g, 140g of water was fed into the magnetic ball mill, preferential grinding of the powder 3 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and coat layer weight 140 g/L catalyst support (A) was obtained. 70g and powder 3 were fed into 70g, 140g of water was fed into the magnetic ball mill, preferential grinding of the powder 2 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to catalyst support (A), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the total coat layer weight 280 g/L catalyst support (B) was obtained. Catalyst support (B) was made to carry out catalyst 1L per 15g sinking-in support of the acetic-acid Ba water solution by oxide conversion, and the exhaust air purification catalyst (C) was acquired to it.

[0065] (Example 5) Except having used the nitric acid Co instead of the nitric acid Fe, the same actuation as an example 1 was repeated, and the exhaust air purification catalyst was acquired (Co/Rh is a mole ratio and is 0.57).

[0066] (Example 6) Except having used the nitric acid nickel for a nitric acid Fe being alike instead, the same actuation as an example 1 was repeated, and the exhaust air purification catalyst was acquired (nickel/Rh is a mole ratio and is 0.57).

[0067] (Example 7) Except having used the nitric acid Mn instead of the nitric acid Fe, the same actuation as an example 1 was repeated, and the exhaust air purification catalyst was acquired (Mn/Rh is a mole ratio and is 0.53).

[0068] (Example 8) 140g and an alumina were fed into 70g, 280g of water was fed into the magnetic ball mill, preferential grinding of 70g and the powder 3 was carried out for the almost same actuation 2 as an example 1, i.e., powder, and slurry liquid was obtained. After having adhered this slurry liquid to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and coat layer weight 280 g/L catalyst support (B) was obtained. Catalyst support (B) was made to carry out catalyst 1L per 15g sinking-in support of the acetic-acid Ba water solution by oxide conversion, and the exhaust air purification catalyst (C) was acquired to it.

[0069] (Example 9) Except having used the zirconium dioxide instead of the activated alumina, the same actuation as an example 1 was repeated, and the exhaust air purification catalyst was acquired.

[0070] (Example 4 of a comparison) a nitric-acid Rh water solution -- activated-alumina powder (mean particle diameter of 1 micrometer) -- sinking in -- after desiccation and N -- it calcinated at 400 degrees C 2 inside for 1 hour, and Rh support alumina powder (powder 4) was obtained. Rh concentration of this powder was 2%. It sank into activated-alumina powder, the JIATORO diamine Pt water solution was calcinated at 400 degrees C among after [desiccation] air for 1 hour, and Pt support alumina powder (powder 3) was obtained. Pt concentration of this powder was 2%. 70g and an alumina were fed into 70g, 140g of water was fed into the magnetic ball mill, preferential grinding of the powder 3 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and coat layer weight 140 g/L catalyst support (A) was obtained. 70g and powder 3 were fed into 70g, 140g of water was fed into the magnetic ball mill, preferential grinding of the powder 2 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to catalyst

support (A), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the total coat layer weight 280 g/L catalyst support (B) was obtained. Catalyst support (B) was made to carry out catalyst 1L per 15g sinking-in support of the acetic-acid Ba water solution by oxide conversion, and the exhaust air purification catalyst (C) was acquired to it.

[0071] (Example 5 of a comparison) With powder 1, except having made concentration of a nitric acid Fe 0.2%, the same actuation as an example 1 was repeated, and the exhaust air purification catalyst was acquired.

[0072] (Example 6 of a comparison) With powder 1, except having made concentration of a nitric acid Fe 40%, the same actuation as an example 1 was repeated, and the exhaust air purification catalyst was acquired.

[0073] (Example 7 of a comparison) With powder 1, except having set mean particle diameter of the powder of an activated alumina to 50 micrometers, the same actuation as an example 1 was repeated, and the exhaust air purification catalyst was acquired.

[0074] The exhaust air system of an engine with a displacement [<the example of an evaluation trial> and durable approach displacement] of 4400 cc was equipped with the exhaust air purification catalyst, catalyst inlet temperature of the preceding paragraph was made into 700 degrees C, and it operated for 30 hours.

- The exhaust air system of the engine of the evaluation approach diesel power plant was equipped with the exhaust air purification catalyst, catalyst inlet temperature was made into 300 degrees C, and it operated for 15 minutes. The exhaust air purification catalyst was attached in the exhaust air system of a gasoline engine, and it considered as A/F=50 and the inlet temperature of 300 degrees C, and operated for 10 minutes. In addition, it asked for the NOx invert ratio by the following formula

$$\text{NOx invert ratio} = (\text{amount of 1-catalyst outlet NOx} / \text{amount of catalyst inlet-port NOx}) \times 100\%.$$

[0075]

[Table 1]

	貴金属		元素		M/Rh(モル比)	Rh担持多孔質体種	多孔質体の 粒子系
	Pt g/L	Rh g/L	M	g/L			
実施例4	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1 μm
実施例5	2.8	1.4	Co	1.4	0.57	Al ₂ O ₃	1 μm
実施例6	2.8	1.4	Ni	1.4	0.57	Al ₂ O ₃	1 μm
実施例7	2.8	1.4	Mn	1.4	0.53	Al ₂ O ₃	1 μm
実施例8	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1 μm
実施例9	2.8	1.4	Fe	1.4	0.54	ZrO ₂	1 μm
比較例4	2.8	1.4	なし	0	0.54	Al ₂ O ₃	1 μm
比較例5	2.8	1.4	Fe	0.14	0.054	Al ₂ O ₃	1 μm
比較例6	2.8	1.4	Fe	28.0	10.8	Al ₂ O ₃	1 μm
比較例7	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	20 μm

[0076]

[Table 2]

	転化率% NOx
実施例4	82
実施例5	80
実施例6	80
実施例7	77
実施例8	79
実施例9	80
比較例4	50
比較例5	60
比較例6	68
比較例7	68

[0077] As shown in Table 1 and 2, the above-mentioned evaluation trial shows that an NOx invert ratio is good in the examples 4-9, even if it is comparatively low temperature exhaust air. On the other hand, in the examples 4-7 of a comparison, it turns out that an NOx invert ratio is bad.

[0078] As mentioned above, although the suitable example and the example of a comparison explained this invention to the detail, this invention is not limited to these examples and various deformation is possible for it within the limits of the summary of this invention. For example, as for the catalyst of this invention, it is desirable to make integral-construction mold support support and to use. As integral-construction mold support, the monolith support which consists of a heat-resistant ingredient can use products made from a ceramic, such as a KODI light, and metal support, such as ferrite system stainless steel, desirably. Moreover, the rate of exhaust air purification of NOx and PM can be raised by distinguishing a catalyst by different color with on support.

[0079]

[Effect of the Invention] As explained above, according to this invention, it writes [once changing C solid particulate in PM (party curate particle) into a hydrocarbon or hydrogen, raising the rate of contact (collision) of a catalyst component and PM particle, and promoting this conversion reaction, and]. The exhaust air purification approach which can carry out self-consecration of NOx and the PM continuously under the usual combustion conditions, without needing specific control, an exhaust air purification catalyst, and an exhaust emission control device can be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows HC generation behavior from C by model gas evaluation trial.

[Drawing 2] It is the graph which shows the NOx reduction purification property by model gas evaluation trial.

[Drawing 3] It is the schematic diagram showing the example of a configuration of an exhaust emission control device.

[Drawing 4] It is the schematic diagram showing other examples of a configuration of an exhaust emission control device.

[Translation done.]

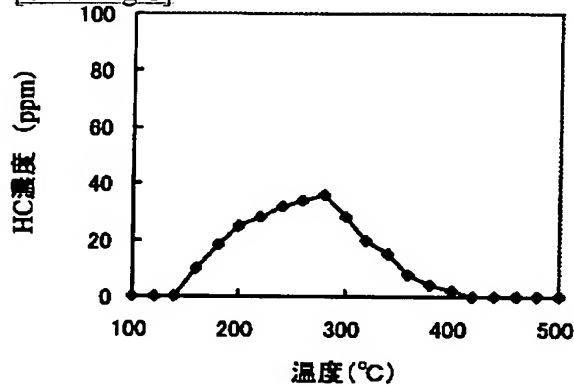
* NOTICES *

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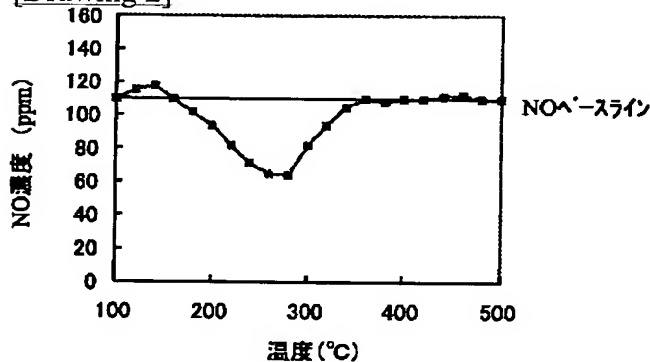
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DRAWINGS

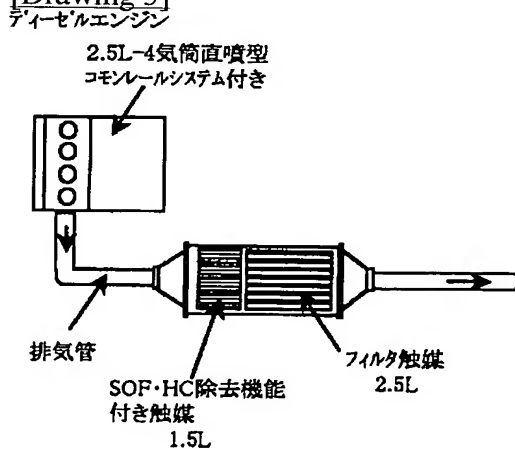
[Drawing 1]



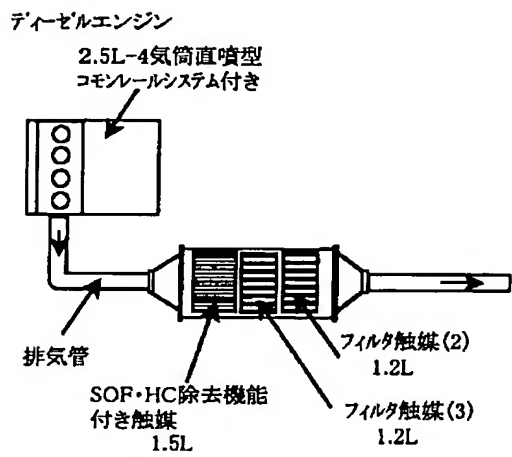
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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(54) 【発明の名称】 排気浄化方法及び排気浄化装置

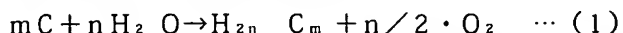
(57) 【要約】

【課題】 通常の燃焼条件の下で、特定の制御を必要とせずにNO_xとPMを連続的に自己浄化することが可能な排気浄化方法、排気浄化触媒及び排気浄化装置を提供すること。

【解決手段】 $mC + nH_2O \rightarrow H_{2n}C_m + n/2 \cdot O_2$ で表される反応によりPM粒子をHCに変換して排気中のPM粒子及びNO_xを浄化する方法である。モノリス型フィルタの気孔内壁に、貴金属と、平均粒径が1μm以下の酸化物微粒子と、を担持したフィルタを排気煙道に配設した排気浄化装置である。排気温度が500℃以下のときに、 $C + H_2O \rightarrow H_2 + CO$ 、 $C + 2H_2O \rightarrow 2H_2 + CO_2$ で表される水素生成反応を行い排気浄化する方法である。H₂生成触媒及びNO_x浄化触媒を含み、H₂生成触媒が、Rhを担持した多孔質粒子と、Fe、Co、Mn及びNiなどの金属とを含み、これら金属はRhを1としたときに0.1～10の比率で含まれる排気浄化触媒である。

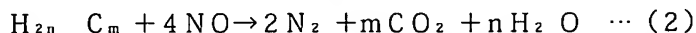
【特許請求の範囲】

【請求項1】 排気中のパーティキュレート粒子及び窒素*



で表される反応によりパーティキュレート粒子を炭化水素に変換する過程を含むことを特徴とする排気浄化方法。

※



で表される反応により窒素、二酸化炭素及び水に変換する過程を含むことを特徴とする請求項1に記載の排気浄化方法。

【請求項3】 上記反応式1で表される反応を、350℃以下の温度で行うことを特徴とする請求項1又は2に記載の排気浄化方法。

【請求項4】 上記反応式1で表される反応を、280℃以下の温度で行うことを特徴とする請求項3に記載の排気浄化方法。

【請求項5】 上記反応式2で表される反応を、350℃以下の温度で行うことを特徴とする請求項1～4のいずれか1つの項に記載の排気浄化方法。

【請求項6】 上記反応式2で表される反応を、280℃以下の温度で行うことを特徴とする請求項5に記載の排気浄化方法。

【請求項7】 請求項1～6のいずれか1つの項に記載の排気浄化方法を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、モノリス型フィルタの気孔内壁に、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも1種の貴金属成分と、平均粒径が1μm以下であるアルミナ、チタニア、ジルコニア及びシリカから成る群より選ばれた少なくとも1種の酸化物微粒子と、を担持して成る触媒機能付きフィルタを内燃機関の排気煙道に配設したことを特徴とする排気浄化装置。

【請求項8】 上記酸化物微粒子の平均粒径が0.6μm以下であることを特徴とする請求項7に記載の排気浄化装置。

【請求項9】 上記モノリス型フィルタの気孔率が30～80%であり、平均気孔径が5～40μmであることを特徴とする請求項7又は8に記載の排気浄化装置。

【請求項10】 上記触媒機能付きフィルタが、2段以上に分割され直列に配置されて成ることを特徴とする請求項7～9のいずれか1つの項に記載の排気浄化装置。

【請求項11】 排気上流側の触媒機能付きフィルタの圧力損失が、排気下流側の触媒機能付きフィルタの圧力損失より大きいことを特徴とする請求項10に記載の排気浄化装置。

【請求項12】 排気上流側の触媒機能付きフィルタの平均気孔径が、排気下流側の触媒機能付きフィルタの平均気孔径より大きいことを特徴とする請求項10又は11に記載の排気浄化装置。

【請求項13】 排気上流側の触媒機能付きフィルタの

* 窒素酸化物を浄化する方法であって、次の反応式1

※【請求項2】 上記炭化水素を窒素酸化物と反応させ、次の反応式2

10 気孔率が、排気下流側の触媒機能付きフィルタの気孔率より大きいことを特徴とする請求項10～12のいずれか1つの項に記載の排気浄化装置。

【請求項14】 上記排気上流側の触媒機能付きフィルタが、衝突濾過機能を有することを特徴とする請求項10～13のいずれか1つの項に記載の排気浄化装置。

【請求項15】 上記排気下流側の触媒機能付きフィルタが、表面濾過機能を有することを特徴とする請求項10～14のいずれか1つの項に記載の排気浄化装置。

20 【請求項16】 上記排気上流側の触媒機能付きフィルタが、セラミック繊維の織布及び／又は不織布を用いて成ることを特徴とする請求項10～15のいずれか1つの項に記載の排気浄化装置。

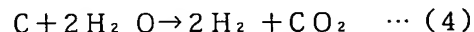
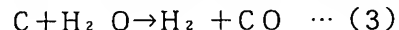
【請求項17】 上記排気下流側の触媒機能付きフィルタが、セラミック焼結体を用いて成ることを特徴とする請求項10～16のいずれか1つの項に記載の排気浄化装置。

【請求項18】 上記触媒機能付きフィルタの排気上流側に、炭化水素及び可溶性有機成分を除去する機能を有するHC・SO_F除去材料を配設して成ることを特徴とする請求項10～17のいずれか1つの項に記載の排気浄化装置。

30 【請求項19】 上記HC・SO_F除去材料が、モルデナイト、MFI、β型ゼオライト、平均細孔径が1～5nmであるシリカ、及び層状粘土鉱物から成る群より選ばれた少なくとも1種のゼオライト及び／又はシリカ含有無機物であることを特徴とする請求項18に記載の排気浄化装置。

【請求項20】 請求項7～19のいずれか1つの項に記載の排気浄化装置を製造する方法であって、上記モノリス型フィルタの気孔内壁に上記酸化物微粒子を分散担持させた後に、上記貴金属成分を含浸法及び／又はメッキ法によって担持させることを特徴とする排気浄化装置の製造方法。

【請求項21】 排気中のパーティキュレート粒子及び窒素酸化物を浄化する方法であって、内燃機関から排出される排気の温度が500℃以下のときに、次の反応式3及び／又は4



で表される水素生成反応を行う過程を含むことを特徴とする排気浄化方法。

50 【請求項22】 請求項21に記載の排気浄化方法に用

いられる水素生成触媒及び窒素酸化物浄化触媒を含む排気浄化触媒であって、

上記水素生成触媒が、少なくともロジウムを担持した多孔質粒子の粉末と、鉄、コバルト、マンガン及びニッケルから成る群より選ばれた少なくとも1種の金属とを含み、これら金属はロジウムを1としたときに0.1～1.0の比率で含まれることを特徴とする排気浄化触媒。

【請求項23】 上記多孔質粒子の平均粒子径が、0.1～2.0 μmであることを特徴とする請求項22に記載の排気浄化触媒。

【請求項24】 請求項22又は23に記載の排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道の上流側に上記水素生成触媒を配設し、その下流側に上記窒素酸化物浄化触媒を配設して成ることを特徴とする排気浄化装置。

【請求項25】 請求項22又は23に記載の排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道上に上記窒素酸化物浄化触媒の積層体を配設し、その上に上記水素生成触媒を被覆して成ることを特徴とする排気浄化装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、排気浄化方法、排気浄化触媒及び排気浄化装置に係り、更に詳細には、内燃機関などから発生する排気中のパーティキュレート(PM)粒子と窒素酸化物(NO_x)を高効率で浄化し得る排気浄化方法、排気浄化触媒及び排気浄化装置に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】近年、燃費向上及び二酸化炭素排出量の削減の観点から、理論空燃比より高い空燃比でも運転するリーンバーンエンジンが普及してきている。特に、ディーゼルエンジンは、その低燃費のゆえに改めて注目されている。

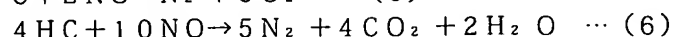
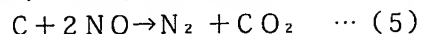
【0003】しかしながら、排気中に固体粒子分であるPMを含み、且つ排気温度が低いことから、従来型の触媒では高効率の排気浄化が困難な状況にある。昨今はエンジンの燃費向上技術が格段に進歩し、排気温度が更に低下する傾向にあるために、排気の浄化は、ますます困難となってきており、ディーゼルエンジンの排気中の有害成分を高効率で浄化できる有効な方法が望まれている。従来のディーゼルエンジンの排気浄化用触媒としては、白金(Pt)をアルミナ(Al₂O₃)等の耐火性高表面積無機担体材料に担持してなる酸化触媒が用いられているが、COとHCの酸化が主機能であり、SOF分もある程度は酸化できるものの、PMの主成分であるドラ

* イースト(C=炭素粒子)の浄化には効力を示さない。

【0004】ディーゼルエンジンの排気のようにPM分を含有する排気を浄化するには、フィルタ技術が不可欠であり、コーゼライトや炭化珪素から成る多孔質焼結体や繊維状のフィルタが多数提案されている。なお、上記繊維状フィルタの素材としては、アルミナやシリカ等各種材料からなるものも提案されている。また、自動車技術会 学術講演会前刷集 No. 103-98(1998年秋季大会)には、炭化珪素繊維を用いたディーゼル・パーティキュレート・フィルタ(DPF)が提案されているが、トラップしたPMを除去してフィルタを再生するためのヒーターが不可欠であり、複雑なシステムが必要であることから、搭載スペースが少ない乗用車には適用が困難である。

【0005】また、ヒーターを用いなくてフィルタを再生する方法として、フィルタの前段にPt系触媒を配置させることによって排気中のNOを酸化力の強いNO₂に転化し、このNO₂の酸化力を利用してフィルタにトラップしたPM分を燃焼する方法が提案されている(特開平1-318715号公報, J. P. Warren, et. al., "Effects on after-treatment on particulate matter when using the Continuously Regenerating Trap", ImechE 1998 S491/006, B. Carberry, et. al., "A focus on current and future particulate after-treatment systems", ImechE 1998 S491/007)。この方法は、排気中の成分同士の反応を利用したもので、トラップしたPM分を連続的に燃焼浄化できることから、連続再生式トラップと呼ばれている。しかし、PM中のカーボン(C)は固体粒子であるために、NO₂との反応速度は比較的遅く、エンジンから排出されたCを十分な速度で燃焼させるためには、排気条件が400℃以上の比較的高い温度条件を要すること、更には、そのような温度域で酸化剤となるNO₂量を増加することが必要となる。即ち、エンジンからのNO_x排出量を増やすことが必要になり、その結果、増えたNO_xを浄化するために高性能のNO_x触媒が必要となる。

【0006】PMとNO_xを同時に浄化するための各種方法も提案されている。例えば、特開平7-116519号公報には、多孔質フィルタにペロブスカイト構造を有する触媒を担持してなる排ガス浄化材が提案されており、これは排ガス中に含まれる微粒子状物質及び/又は炭化水素を還元剤として作用させ、排気中の窒素酸化物を還元する方法であり、該触媒を用いた下記反応式5及び



で表される反応によりNO_xを還元するとされている。上記反応において、反応式6は気体分子同士の反応であることから触媒作用が期待されるのに対し、反応式5は固体と気体との反応であるため触媒作用を期待することは難しく、通常の走行モード条件下でフィルタ再生ができるかは不明である。

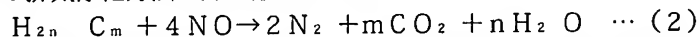
【0007】一方、特許掲載第2722987号公報には、NO_x吸収剤とフィルタを伝熱可能な位置に配置してNO_x吸収剤からNO_x放出還元後にPMを燃焼させることが提案されている。また、特開平9-94434号公報には、NO_x吸収剤をウォールフロー型フィルタの隔壁気孔内部に担持して、フィルタとNO_x吸収剤を一体化した触媒が提案されている。

【0008】これらはNO_xを処理する触媒とフィルタとを組み合わせ得られる技術であり、NO_x処理とPM燃焼のためにそれぞれ別のエンジン制御を必要とする。NO_x吸収剤を働かせてNO_xを吸収、還元するためには排気の空燃比(A/F)を変える制御が必要である。また、フィルタを再生させるための堆積PMの燃焼、及びNO_x吸収剤にトラップされた硫黄化合物の除去には、NO_x吸収剤及び／又はフィルタを600℃あるいはそれ以上にまで昇温させる必要があり、更にNO_x吸収剤からの硫黄化合物の除去は還元雰囲気下で行うのに対し、フィルタの再生は酸化雰囲気条件で行うことが必要である。更にまた、高温化により触媒の劣化を促進し、システム的にも高コスト化するという問題点がある*



で表される反応によりパーティキュレート粒子を炭化水素に変換する過程を含むことを特徴とする。

【0012】また、本発明の排気浄化方法の好適形態 ※30



で表される反応により窒素、二酸化炭素及び水に変換する過程を含むことを特徴とする。

【0013】更に、本発明の排気浄化装置は、上記排気浄化方法を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、モノリス型フィルタの気孔内壁に、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも1種の貴金属成分と、平均粒径が1μm以下であるアルミナ、チタニア、ジルコニア及びシリカから成る群より選ばれた少なくとも1種の酸化物微粒子と、を担持して成る触媒機能付きフィルタを内燃機関の排気煙道に配設したことを特徴とする。

【0014】更にまた、本発明の排気浄化装置の好適形態は、上記モノリス型フィルタの気孔率が30～80%であり、平均気孔径が5～40μmであることを特徴とする。

【0015】また、本発明の排気浄化装置の他の好適形態は、上記触媒機能付きフィルタが、2段以上に分割され直列に配置されて成ることを特徴とする。

【0016】更に、本発明の排気浄化装置の更に他の好

*る。このような排気温度や雰囲気(A/F)の制御は複雑であり、また、燃費や運転性の犠牲を伴うことから、通常の走行条件下で特定の制御を加えることなく連続的に自己浄化可能な排気浄化方法が切望されている。また、PM、NO_xの同時除去を目的に、フィルタに触媒を担持する提案がなされているが、触媒成分とPM粒子との接触あるいは衝突確率という観点からの工夫はなれていなかった。

【0009】本発明は、このような従来技術にの有する課題に鑑みてなされたものであり、その目的とするところは、通常の燃焼条件下で、特定の制御を必要とせずにNO_xとPMを連続的に自己浄化することが可能な排気浄化方法、排気浄化触媒及び排気浄化装置を提供することにある。

【0010】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく鋭意検討を重ねた結果、PM中のC固体粒子(パーティキュレート粒子)を一旦炭化水素や水素に変換すること、触媒成分とPM粒子との接触(衝突)率を高めて該変換反応を促進させることにより、上記課題が解決できることを見出し、本発明を完成するに至った。

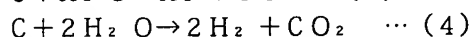
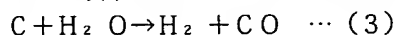
【0011】即ち、本発明の排気浄化方法は、排気中のパーティキュレート粒子及び窒素酸化物を浄化する方法であって、次の反応式1

※は、上記炭化水素を窒素酸化物と反応させ、次の反応式2

適形態は、上記触媒機能付きフィルタの排気上流側に、炭化水素及び可溶性有機成分を除去する機能を有するHC・SOF除去材料を配設して成ることを特徴とする。

【0017】更にまた、本発明の排気浄化装置の製造方法は、上記排気浄化装置を製造する方法であって、上記モノリス型フィルタの気孔内壁に上記酸化物微粒子を分散担持させた後に、上記貴金属成分を含浸法及び／又はメッキ法によって担持させることを特徴とする。

【0018】また、本発明の他の排気浄化方法は、排気中のパーティキュレート粒子及び窒素酸化物を浄化する方法であって、内燃機関から排出される排気の温度が500℃以下のときに、次の反応式3及び／又は4



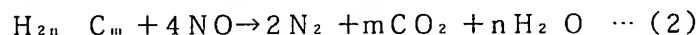
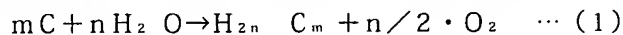
で表される水素生成反応を行う過程を含むことを特徴とする。

【0019】更に、本発明の排気浄化触媒は、上記排気浄化方法に用いられる水素生成触媒及び窒素酸化物浄化触媒を含む排気浄化触媒であって、上記水素生成触媒

が、少なくともロジウムを担持した多孔質粒子の粉末と、鉄、コバルト、マンガン及びニッケルから成る群より選ばれた少なくとも1種の金属とを含み、これら金属はロジウムを1としたときに0.1～10の比率で含まれることを特徴とする。

【0020】更にまた、本発明の他の排気浄化装置は、上記排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道の上流側に上記水素生成触媒を配設し、その下流側に上記窒素酸化物浄化触媒を配設して成ることを特徴とする。

【0021】また、本発明の更に他の排気浄化装置は、上記排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道上に上記窒素酸化物浄化触媒の積層体を配設し、その上に上記水素生成触媒を被覆して成ることを特



で表される変換反応を進行させることでNO_x及びPMがほぼ同時に除去される。ここで、CとH₂OによるHC生成反応(式1)において、PM中のCがHCに変換されるメカニズムの詳細は現時点では不明であるが、本発明者らは、例えば、Pt/アルミナ系触媒を、C(グラファイト)/O₂/H₂O/N₂系のモデルガスと反応させた評価を行い、図1のグラフに示すように、HCを検出した。また、モデルガス中にNOを追加導入して評価を行い、図2に示すように、NO濃度が減少することを確認した。従って、HC生成反応(式1)及びHC-NO反応(式2)が起こっていることが推察できる。

【0025】更に、上記HC生成反応(式1)及びHC-NO反応(式2)を進行させるには、一例である図1及び図2のグラフからもわかるように、温度条件を350℃以下とすることが好ましく、特に280℃以下とすることがより好ましい。なお、下限温度は、触媒の性能などにより異なるが、概ね200℃以上の温度であれば顕著な反応速度が得られる。ここで、350℃より高い温度条件では、上記HC生成反応(式1)で生成したHCの酸化反応が優勢となり、上記HC-NO反応(式2)も劣勢となると考えられる。一方、酸素の多い排気条件(リーンバーンエンジンなど)におけるPt系触媒上でのHC-NO_x反応(式2)は、概ね150℃～300℃の温度域で顕著に進行することが知られている。このように、本発明の排気浄化方法を用いれば、上記HC生成反応(式1)及びHC-NO反応(式2)を比較的低温条件で進行させ得るので、PMが重大な問題となっているディーゼルエンジンからの排気を特定のエンジン制御を行わずに高効率で浄化できる。

【0026】次に、本発明の排気浄化装置について詳細に説明する。上述のHC生成反応(式1)や上記HC-NO反応(式2)を進行させるには、触媒を使用するこ

* 徴とする。

【0022】

【発明の実施の形態】以下、本発明の排気浄化方法について詳細に説明する。なお、本明細書において「%」は特記しない限り、質量百分率を示す。

【0023】本発明の排気浄化方法は、排気中のパーティキュレート(PM)粒子及び窒素酸化物(NO_x)を浄化する方法であって、PM粒子を炭化水素(HC)に変換することにより、通常の走行条件では燃焼し難い排気中のPM粒子を高効率で浄化することを特徴とする。また、生成したHCを排気中のNO_xと反応させることで、NO_xは無害な窒素(N₂)、CO₂及びH₂Oに変換される。なお、生成したHCは、直ちに酸化して二酸化炭素(CO₂)や水(H₂O)に変換しても良い。

【0024】即ち、本発明の排気浄化方法では、次の反応式1及び2

とが必須条件であるが、本発明者らは、かかる反応では触媒とPM粒子とが直接接触することが大変有効であることを知見した。例えば、上記HC生成反応(式1)は、Pt/アルミナ系触媒粉末とカーボン(C)粉末とを十分に良く混合した場合にのみ進行し、混合が不十分な場合には進行しない。本発明の排気浄化装置は、かかる観点から触媒成分とPM粒子との接触(衝突)確率を高める手段として、濾過機能を積極的に利用する。即ち、濾過機能及び触媒機能を有する排気浄化装置とし、フィルタの気孔内壁表面上に触媒成分を分散、担持させることで、狭い気孔内に流入してくるPM粒子と触媒成分との接触(衝突)確率を高める。なお、上記触媒成分の担持方法としては、後述するように、メッキ法などにより内壁一面を被覆する担持方法が有効である。

【0027】ここで、本発明の排気浄化装置は、具体的には、モノリス型フィルタの気孔内壁に、上記触媒成分として、白金(Pt)、パラジウム(Pd)又は(Rh)、及びこれらの任意の組合せより成る貴金属成分を担持させて成る。このとき、貴金属成分は、特に単独で使用する必要はなく、2成分以上を組合せて使用するときには、上記HC生成反応(式1)及びHC-NO反応(式2)をより円滑に進めることができる。例えば、PtとRhの組合せでは、PtでHC生成反応(式1)を促進させ、RhでHC-NO反応(式2)を促進させることができる。

【0028】また、上記モノリス型フィルタの気孔内壁には、平均粒径が1μm以下の微粉の酸化物粒子、具体的には、貴金属成分の担体として従来から用いられているアルミナ(Al₂O₃)、チタニア(TiO₂)、ジルコニア(ZrO₂)又はシリカ(SiO₂)、及びこれらの任意の組合せに係る酸化物微粒子を担持させる。これより、気孔が閉塞されず、気孔内壁の表面に触媒成

分が良好に分散する。更に、上記平均粒径は $0.6\mu\text{m}$ 以下であることがより好ましい。更にまた、上記酸化物微粒子は、単独でも使用できるが、2種以上の触媒成分を担持するときなどは2種以上の酸化物微粒子を組合せて使用するとより効果的なことがある。なお、平均粒径が $1\mu\text{m}$ を超えると上記モノリス型フィルタの気孔が閉塞されてしまうことがある。また、上記酸化物微粒子は、該酸化物微粒子を生成し得る水酸化物や硝酸塩の水溶液をフィルタの気孔内壁に浸透させ、分散担持させることができる。

【0029】更に、上記貴金属成分や酸化物微粒子の担持方法としては、酸化物微粒子の粉末をフィルタ気孔内壁に浸透担持させ、次いで貴金属成分を担持させる方法や、貴金属成分を予め酸化物微粒子に担持させた後、該酸化物微粒子をフィルタ気孔内壁に浸漬担持させる方法などが例示できる。特に、貴金属成分をできるだけ粒子表面側に露出させるには、前者がより有効である。

【0030】更にまた、上記貴金属成分や酸化物微粒子の担体としては、濾過機能を有するモノリス型のフィルタを使用する。このとき、該モノリス型フィルタは、フィルタとしての基本特性が優れていること、即ち、高捕集率・高捕集量・低圧損であることが望ましい。また、触媒成分（貴金属成分）を気孔内壁表面に担持でき、この触媒成分を排気中のPM粒子と高い確率で接触させ得ることがよい。

【0031】また、上記モノリス型フィルタにおいて、気孔率は30～80%であることが好適である。気孔率が30%未満であると、所定の性能を満たすためのフィルタサイズを大きくとらなくてはならず、搭載性が悪化することがある。また、80%を超えると強度が低下し、搭載性が悪化することがある。更に、気孔径は平均気孔径で5～40 μm であることが好適である。このときは、気孔の大きさが担持する触媒成分の粒径に適切であり、PM粒子が容易に侵入可能となり気孔壁との接触確率を増大できるので有効である。5 μm より小さいとPM粒子の侵入が困難となり、侵入しても気孔内を移動し難いことがある。一方、40 μm より大きいとPM粒子と気孔壁との接触確率が低下し、反応せずに気孔内を通過してしまうことになる。

【0032】更にまた、上記モノリス型フィルタとしては、コーゼライト、ムライト及びSiC等のセラミック焼結体や、セラミック繊維（ファイバ）の織布及び／又は不織布などを用いることができる。また、フィルタ形状は、例えば、上記セラミック焼結体であればハニカム交互目詰めタイプ、上記セラミック繊維の織布や不織布であれば何らかの基材に巻いたり所望形状に成形したものなどを挙げることができる。なお、上記モノリス型フィルタは、特に限定されないが、それぞれの特性に合わせて使い分けことが重要である。例えば、ファイバから成るフィルタは、捕集効率を高めるには不利である

が、気孔径分布を比較的広くすることが可能であり、幅広いPM粒子径の排気に適用し易い。特に、ファイバは比較的フレキシブルであるためPM粒子との接触確率が高く、より反応し難い大きなPM粒子の処理に有効である。また、フィルタを2段以上に分割配置する場合は、排気上流側にセラミック繊維の織布及び／又は不織布を用いたフィルタを配設することがよく、排気下流側にセラミック焼結体を用いたハニカム型フィルタを配設することがよい。なお、ハニカム型フィルタは、比較的小サイズでも接触面積が大きく取れるため、低圧損—高捕集量—高捕集率の代表的なフィルタである。

【0033】また、上記モノリス型フィルタに触媒成分を担持させた触媒機能付フィルタは、2段以上に分割して配置することが好適である。この場合は、排気上流側と下流側とで特性の違った触媒機能付フィルタを配置できるので有効である。例えば、図4に示すように、上記触媒機能付フィルタを2段に分割し直列に配置することができる。これより、PM粒子の気孔通過距離を稼ぐことができ、触媒成分が担持されたフィルタ気孔内壁へのPM粒子の衝突回数が増大するため、上記HC生成反応（式1）や上記HC—NO反応（式2）の効率が大幅に向上し得る。

【0034】更に、上記分割配置した触媒機能付フィルタでは、排気上流側のフィルタの圧力損失を排気下流側のフィルタの圧力損失より大きくすることが好適である。通常、分割配置は圧力損失を高めてしまうが、この場合は、その影響を抑えることができる。これはPM粒子と触媒成分との接触確率を高める上でも重要であり、上流側のフィルタでPM粒子の大部分を捕捉すると、反応速度よりも堆積速度が優勢となり、フィルタが閉塞し易い。なお、フィルタの圧力損失は、フィルタの気孔率や平均気孔径などを変更して制御できる。その結果、PM捕集率も変更できる。

【0035】更にまた、PM捕集率の面から、排気上流側には比較的捕集率の低いフィルタを配置し、排気下流側には捕集率の高いフィルタを配置することが好ましい。言い換えれば、排気上流側のフィルタの平均気孔径や気孔率を、排気下流側のフィルタの平均気孔径や気孔率より大きくすることがよい。この場合は、HC生成に対するC粒子の有効利用率が高められ、NO_x浄化率が向上し得る。

【0036】このとき、排気上流側のフィルタには、比較的大きな粒径のPM粒子が捕捉されるが、フィルタ内で触媒成分と接触する度に粒子表面がHCに変換され、粒径を減らしながら気孔内を移動する。しかし、フィルタ内で触媒成分が存在しない部分があると、PM粒子はそこに固定され閉塞の核となってしまうことがある。このため、排気上流側に設置するフィルタは、PM捕集率がむしろ低く、閉塞を起こし難いタイプが有効であり、いわゆる衝突濾過方式の構造を有するフィルタであるこ

とが好ましい。例えば、3次元網目ランダム構造を有するフォーム型、ファイバ型などが挙げられる。特に、上記ファイバ型のフィルタは、触媒成分がコートされた部位がフレキシブルに伸縮可能であるため、ファイバ間に捕捉されたPM粒子は排気圧力によってファイバ粒子を押しつけながら移動できるので、フィルタ気孔が閉塞し難く、また、触媒成分とPM粒子との接触確率が稼げるため、反応が促進され易い。一方、排気下流側には、高捕集率、高捕集量及び低圧損のフィルタを配置することが好適である。排気下流側のPM粒子は、上流側である

程度反応して低サイズ化しているので、確実に捉えて完全に反応させる特性が必要だからである。例えば、表面濾過機能を有するフィルタを用いることができる。

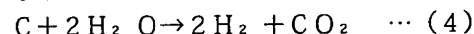
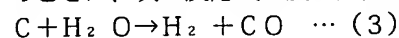
【0037】また、排気中に含まれているHCやSO_Fは、触媒を用いて吸着機能と酸化機能を強化することにより、浄化効率を高めることができるが、フィルタまで到達すると気孔内壁の触媒成分上でNO_xと反応したり、気孔内壁、即ち触媒表面を覆ったりして、触媒作用を妨げるなどの悪影響を及ぼす可能性がある。そこで、HCやSO_F分は、予めフィルタの上流でトラップしておき、フィルタ内でCから生成したHCとNO_xとの選択的反応を促進することが排気浄化作用を発揮させる上で有効である。具体的には、フィルタの排気上流側に、炭化水素及び可溶性有機成分を除去する機能を有するHC・SO_F除去材料を配設することが好ましい。これより、350℃以下の比較的低排温条件でもPMとNO_xの高効率浄化が可能になる。HC・SO_F除去材料は、例えば、図3又は図4に示すように配設できる。また、HC・SO_F除去材料としては、モルデナイト、MF I、β型ゼオライト、平均細孔径が1～5 nmであるシリカ又は層状粘土鉱物、及びこれらの任意の組合せに係るゼオライト及び／又はシリカ含有無機物を好適に使用できる。なお、上記シリカとしては、いわゆるメソポーラスシリカと称せられる酸化物の多孔体が挙げられ、例えば、界面活性剤を鋳型として用いて得ることができる。平均細孔径が1 nm未満では細孔径が小さすぎてHC、SO_F分の十分な吸着捕捉ができず、5 nmを超えると細孔径が大きすぎてHC、SO_F分の吸着効率が低下することがある。また、上記層状粘土鉱物としては、ヘクトライト、モンモリロナイト等が挙げられる。これらの多孔体材料は、フィルタの上流側でHCやSO_Fを高効率で吸着捕捉するとともに、更にPtやPd等の触媒成分を添加することにより、気相酸素を利用した酸化除去が可能となり、フィルタ気孔内壁における生成HCの有効利用率が高められる。上記多孔体材料は、例えば、1平方インチ当たり400個程度の孔を有する、いわゆるフロースルー型のコーゼライト製のハニカム担体にコーティングして用いることができる。該多孔体の粉末をハニカム体にコーティングしてハニカム面に接着・固定させるためには、アルミナゾル、シリカゾルなど

の焼結剤（バインダー）を用いるのが一般的である。また、PtやPd等の触媒成分を添加することにより、多孔体材料に吸着したHCやSO_Fの酸化除去を促進することができる。この場合、該多孔体材料に直接触媒成分を担持させても良いし、アルミナやチタニア等の担体に触媒成分を予め担持させた粉末を多孔材料粉に混合して用いても良い。

【0038】上述した排気浄化装置は、上記モノリス型フィルタの気孔内壁に上記酸化物微粒子を分散担持させた後に、上記貴金属成分を含浸法及び／又はメッキ法によって担持させて得られる。なお、通常の触媒調製法で常用される含浸法も有効であるが、フィルタ気孔内壁を被覆できるメッキ法を用いるのがより効果的であり、更にメッキ法と含浸法とを併用することも有効である。メッキ法としては、各種の方法が有効であり、代表的には電解法や無電解法などを適宜適用できる。

【0039】以上のように、本発明の排気浄化装置は、フィルタに堆積したPMを燃焼させるための各種排気昇温制御、NO_xを除去するための排気A/F変動制御、更にはNO_x吸着機能を使わないため、NO_x吸着触媒からのS脱離制御等の特定の制御を必要とせず、燃費の悪化を抑制できる。また、低温でCを浄化できるため、フィルタの熱による破損の恐れがなく、長期間の使用に耐えられる。例えば、ディーゼルエンジンにおいて、クリーンな排気を実現することができ、地球温暖化の問題を含めて環境汚染が少ない、経済性（燃費）に優れた自動車を提供することができる。

【0040】次に、本発明の他の排気浄化方法、排気浄化触媒及び排気浄化装置について詳細に説明する。かかる排気浄化方法は、触媒に付着した煤（PM粒子）から水素を生成し、その水素を用いてNO_xを浄化する。即ち、内燃機関から排出される排気の温度が500℃以下のときに、次の反応式3及び／又は4



で表される水素生成反応を行う。これより、500℃以下の温度でもPM粒子より水素が生成され、この水素を用いてNO_xを浄化し得る。

【0041】ここで、通常、NO_xの還元剤として排気中のHCやCO、更にH₂を使用する場合、リーン雰囲気では酸素が多く存在するため、これら還元剤はH₂OやCO₂になってしまう。そのため、リーン雰囲気が大部分の運転条件（リーンバーンエンジンなど）の排気を浄化する場合においては、上記水素生成反応（式3及び4）が有効に利用できないという不具合があった。また、酸素過剰のリーン雰囲気では、触媒に付着したPMは水蒸気と水素生成反応（式3及び4）をほとんど行わない。

【0042】本発明の排気浄化触媒は、リッチ又はリーンの雰囲気に関係なく排気中に存在するPMを触媒表面

に付着させる。そして、このPMは、リッチ雰囲気のみならずリーン雰囲気でも、主にRhの作用により水素生成反応(式3及び4)に用いられ、水素が生成する。従って、リーン雰囲気でも生成した水素でNO_xを還元でき、NO_x浄化性能を向上できる。また、硫黄被毒されたNO_x吸着サイトのSO_xも水素によって還元できるため、NO_x吸着能を回復できるとともに新たな硫黄被毒を防止できる。これによってもNO_x浄化性能を向上できる。

【0043】具体的には、上記H₂生成触媒としては、少なくともロジウム(Rh)を担持した多孔質粒子の粉末と、鉄(Fe)、コバルト(Co)、マンガン(Mn)又はニッケル(Ni)、及びこれらの任意の組合せに係る金属とを含むものを用いる。このとき、上記Fe、Co、Mn及びNiなどの金属は上記多孔質粒子に担持されていることがよい。かかるH₂生成触媒を用いることにより、500℃以下の温度でPMとH₂Oから生成させたH₂により高いNO_x浄化性能を発現できる。また、後述するように、更にNO_x吸着材を用いると、リーンでNO_xを吸着するため、PMとH₂Oから生成したH₂とNO_xとの反応性が向上するので、NO_xの浄化反応を促進できる。更に、排気中のSO_xがNO_x吸着サイトと反応して触媒表面にSO_x吸着種やSO_x塩を形成することによりNO_x吸着能が消失してしまう(いわゆる硫黄被毒)場合があるが、上記生成させたH₂によりSO_xが還元されるため硫黄被毒を防止できる。更にまた、硫黄被毒を受けたNO_x吸着サイトもH₂により還元され、NO_x吸着能が復活し易い。

【0044】また、上記H₂生成触媒には、上記Fe、Co、Mn及びNiなどの金属が、Rhを1としたときに0.1~10の比率で含まれる。特に1~5であることがより好ましい。0.1より小さいとこれら金属による効果が現れず、Rhのみの場合と変わらない。一方、10を超えるとRhの活性が低下し、PMとRhの反応性が悪化してしまう。更に、上記Rhは、多孔質粒子120g当たり0.05~20gの範囲で担持されることが望ましい。Rhの担持量が0.05g/120gより少ないと耐久性が低下し易く、20g/120gより多いと上記効果が飽和するとともにコストの増大を招き易い。更に、Rhとともに白金(Pt)、パラジウム(Pd)及びイリジウム(Ir)などを担持することもでき、このときの担持量は、Rhとこれら金属との合計を上記範囲とすればよい。なお、上記多孔質粒子に担持されるPtは、多孔質粒子120g当たり0.1~10gの範囲であることが望ましい。Ptの担持量が0.1g/120gより少ないとHC、CO及びNO_xの浄化率が低下し易く、10g/120gより多くても効果が飽和するとともにコストの増大を招き易い。

【0045】また、上記多孔質粒子としては、例えば、アルミナ、シリカ、チタニア、ジルコニア、シリカーア

ルミナ及びゼオライトなどから適宜選択でき、1種を単独で使用したり、複数の種類を混合又は複合化して使用できる。但し、耐熱性が悪い、ZrはRhと相性が良いなどの理由から、Rh担持粉末にはアルミナ、ジルコニア又はジルコニア-アルミナを用いることが望ましい。更に、上記多孔質粒子の粒径は、0.1~20μmの範囲であることが好ましい。粒径が0.1μmより小さいとRhの分散度が低下し、PMとH₂OからのH₂生成効果が十分に得られにくく、20μmより大きいとRh粉末同士が近接する確率が高くなり、結果としてRhの分散度が低下し、PMとH₂OによるH₂生成効果が十分に得られないことがある。

【0046】なお、上記多孔質粒子に更にNO_x吸着材を担持させることもでき、この場合は、NO_x吸着能を更に向上できる。かかるNO_x吸着剤としては、アルカリ金属、アルカリ土類金属又は希土類金属、及びこれらの任意の組合せに係る金属などを使用できる。具体的には、アルカリ金属としては、リチウム(Li)、ナトリウム(Na)、カリウム(K)及びセシウム(Cs)などが挙げられる。アルカリ土類金属としては、周期表2A族元素であるマグネシウム(Mg)、カルシウム(Ca)、ストロンチウム(Sr)、バリウム(Ba)などが挙げられる。希土類金属としては、ランタン(La)、セリウム(Ce)及びプラセオジウム(Pr)などが挙げられる。また、このNO_x吸着材は、多孔質粒子120g当たり0.05~3.0モルの範囲で担持されることが望ましい。担持量が0.05mol/120gより少ないとNO_x浄化率が低下し易く、3.0mol/120gより多く担持しても効果が飽和し易い。更に、上記多孔質粒子にRh及びPtを担持させたときは、Rhと、Ni、Fe、Co、Mnなどの金属等の作用を充分引き出すために、Rh担持多孔質粒子(第1粉末)とPt担持多孔質粒子(第2粉末)を別々に製造し、その後これらを混合することがよい。この場合、第1粉末と第2粉末の混合比は、RhとPtの重量比換算で第1粉末:第2粉末=0.05:1~1:1の範囲が望ましい。また、第1粉末及び第2粉末がともに多孔質粒子としてアルミナを用いた場合は、アルミナの重量比換算で第1粉末:第2粉末=0.1:1~2:1の範囲が望ましい。これらの範囲から外れると、上記したRh及びPtの過不足の場合と同様の不具合が発生する場合がある。また、上記多孔質粒子に遷移金属を担持させたときは、更にMgを担持させることが望ましい。この助触媒を使用することにより、水素生成反応が促進され易いので有効である。

【0047】本発明では、上述の排気浄化触媒を用いて、排気中のパーティキュレート粒子及び窒素酸化物を浄化する排気浄化装置とすることができる。即ち、本発明の排気浄化装置は、内燃機関の排気煙道の上流側に上記水素生成触媒を配設し、その下流側に上記窒素酸化物

浄化触媒を配設して成る。このような構成とすることで、上記水素生成反応(式3及び4)を促進させる排気浄化装置となる。また、本発明の他の排気浄化装置は、内燃機関の排気煙道上に上記窒素酸化物浄化触媒の積層体を配設し、その上に上記水素生成触媒を被覆して成る。例えば、 NO_x 触媒を多層化し、その最上層にFe、Co、Mn又はNi、及びこれらの任意の組合せから成る金属を含むRh粉末を被覆することができる。

【0048】

【実施例】以下、本発明を実施例及び比較例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0049】以下の実施例1～3及び比較例1～3では、本発明の排気浄化装置、即ち、炭化水素(HC)生成触媒を用いた排気浄化装置について、性能評価試験を行った。

【0050】(実施例1)硝酸アルミニウムの水溶液に平均粒径 $0.5\mu\text{m}$ の超微粒アルミナを分散させて得た硝酸酸性水溶液に、気孔率60%、平均気孔径 $18\mu\text{m}$ であり、1平方インチ当たり約200セルの通気孔を有するコーゼライト製ハニカム型交互目詰めフィルタ2.5Lを浸した後、熱風乾燥-焼成工程を3回繰り返して、フィルタの気孔内壁にアルミナを分散担持させた。このときのアルミナの担持量は、フィルタ容積1L当たり約85gであった。また、このフィルタを、Pt濃度が約2.5%のジニトロジアンミンPt水溶液に浸し、熱風乾燥-焼成工程を2回繰り返して、フィルタの気孔内壁に分散担持させたアルミナにPtを担持させた。更に、このフィルタに無電解メッキを施し、フィルタ触媒1Aを得た。メッキ法は、Ptと還元剤を含むメッキ浴水溶液に上記ハニカムフィルタを浸し、Ptを析出させて得た。このときのPtの担持量は、フィルタ容積1L当たり約10gであった。

【0051】このフィルタ触媒1Aの前段に配置するHC及びSOFを吸着除去する機能を有するハニカム状モノリス材(ハニカム触媒1B)を次のようにして得た。含浸法によって比表面積約 $220\text{m}^2/\text{g}$ の γ アルミナを主成分とする活性アルミナにPtを2.5%担持させて得たPt/ γ アルミナ粉末を、比表面積約 $830\text{m}^2/\text{g}$ 、平均細孔径約3.2nmのポーラスシリカと、比表面積 $450\text{m}^2/\text{g}$ でシリカアルミナ比約90のゼオライト β 、更に比表面積 $350\text{m}^2/\text{g}$ でシリカアルミナ比約70のMFIゼオライトを重量比1:4:1で混合し、ベーマイト粉末とともに5:6:1の重量比で混合し、更に硝酸酸性アルミナゾルを1%加え、水と混合してスラリー液を得た。該スラリーを1平方インチ当たり400セルの通気孔を有するコーゼライトハニカム1.5Lにコーティングし、乾燥、焼成の過程を経て、HC、SOFを吸着・分解する機能を有するハニカム触媒1Bを得た。上記、ハニカム触媒1Bとフィルタ触媒

1Aとを、それぞれ前段、後段に組み合わせて、一つのコンバーターに組み込むことにより、排気浄化装置1を得た。

【0052】(実施例2)前段にハニカム触媒を設置せず、フィルタ触媒2Aのみとした以外は、実施例1と同様の操作を繰り返して、排気浄化装置2を得た。

【0053】(実施例3)気孔率60%、平均気孔径 $18\mu\text{m}$ であり、1平方インチ当たり約200セルの通気孔を有するコーゼライト製ハニカム型交互目詰めフィルタ1.25Lと、気孔率65%、平均気孔径 $32\mu\text{m}$ であり、1平方インチ当たり約200セルの通気孔を有するコーゼライト製ハニカム型交互目詰めフィルタ1.25Lとを用意し、実施例1とほぼ同様の操作を繰り返して、2つのフィルタ触媒3A₁及び3A₂を得た。これらのフィルタ触媒3A₁及び3A₂とハニカム触媒3Bを直列に配置して、排気浄化装置3を得た。即ち、これら触媒は、排気上流側から、ハニカム触媒3B-フィルタ触媒3A₂-フィルタ触媒3A₁の順に配置した。

【0054】(比較例1)含浸法によって比表面積約 $220\text{m}^2/\text{g}$ の γ アルミナを主成分とする活性アルミナにPtを2.5%担持させて得たPt/ γ アルミナ粉末を、ベーマイト粉末と10:2の重量比で混合し、更に硝酸酸性アルミナゾルを1%加え、水と混合してスラリー液を得た。該スラリーを1平方インチ当たり400セルの通気孔を有するコーゼライトハニカム1.5Lに $100\text{g}/\text{L}$ コーティングし、乾燥、焼成の過程を経て、ハニカム状酸化触媒R1Bを得た。このハニカム状酸化触媒R1Bと、気孔率60%、平均気孔径 $18\mu\text{m}$ であり、1平方インチ当たり約200セルの通気孔を有するコーゼライト製ハニカム型交互目詰めフィルタ2.5Lを直列に配置し、一つのコンバーターに組み込むことにより、比較例1になる排気浄化装置R1を得た。なお、この装置R1は、いわゆる従来の連続再生式トラップと類似の構成を有する。

【0055】(比較例2)比較例1と同じPt/ γ アルミナ触媒のスラリーを、実施例1と同じコーゼライト製ハニカム型交互目詰めフィルタ2.5Lにコーティングし、熱風乾燥-焼成工程を4回繰り返すことによりフィルタの片側にPt/アルミナ触媒を担持させて、フィルタ触媒R2Aを得た。このときのPt/アルミナ触媒の担持量は、フィルタ容積1L当たり約100gであった。このフィルタ触媒R2Aのみで、排気浄化装置R2を得た。なお、この排気浄化装置R2は、実施例2の排気浄化装置2と比較して、フィルタ触媒の製法を変えたもの、即ち、フィルタ内壁表面にはPt/アルミナ触媒を担持させず、フィルタ外壁に触媒層を形成したものである。

【0056】(比較例3)比較例2と同じフィルタ触媒R2Aの前段に実施例1と同じハニカム触媒1Bを配置

させて、一つのコンバーターに組み込むことにより、排気浄化装置R3を得た。

【0057】＜評価試験例＞コモンレールシステムを備えた4気筒2.5Lの直噴型ディーゼルエンジンを設置したエンジンダイナモ装置を用いて、実施例及び比較例の排気浄化装置の性能評価試験を行った。なお、本評価装置は、触媒システム入口の排気温度を、エンジンの負荷、吸気絞り及びコモンレールシステムによるポスト噴射により制御できるものを用いた。また、排気浄化装置の性能評価法は、装置の入口温度を250℃で2分保持し、次いで300℃で3分保持し、更に350℃で1分間保持するパターンを5時間繰り返す過渡性能評価法を用いた。なお、本評価試験では、スウェーデンクラス1軽油を用いた。

【0058】上記評価試験において、排気浄化装置1（実施例1）について、PM及びNO_xの平均低減率を算出したところ、PM除去率は93%、NO_x除去率は46%であった。また、初期に対する5時間運転後の圧力損失上昇は、25mmHgであった。同様に、排気浄化装置2（実施例2）に関しては、運転2時間における低減率は、PM除去率が90%、NO_x除去率が55%であった。また、初期に対する4時間運転後の圧力損失上昇は、32mmHgであり、PM中のSOFによる触媒成分の被覆が起り酸化性能が経時的に低下したものである。これより、排気浄化装置1のように、前段側でSOF分を除去することにより触媒の被覆を防止し、耐久性が高まることがわかる。また、排気浄化装置3（実施例3）に関しては、PM除去率が95%、NO_x除去率が57%であった。また、初期に対する5時間運転後の圧力損失上昇は、18mmHgであった。これより、フィルタを分割した効果が発揮されていることがわかる。

【0059】一方、排気浄化装置R1（比較例1）に関しては、PM除去率が95%、NO_x除去率が2%であり、NO_x低減率が実施例に比べて低く、また、運転3時間後の圧力損失上昇が40mmHgを超えてしまいエンジン負荷が大きくなったために、その時点で運転を取りやめた。また、排気浄化装置R2（比較例2）に関しては、PM除去率が92%、NO_x除去率が8%であり、また、初期に対する運転3時間後の圧力損失上昇が40mmHgを超えてしまいエンジン負荷が大きくなったために、その時点で運転を取りやめた。更に、排気浄化装置R3（比較例3）に関しては、PM除去率が92%、NO_x除去率が11%であり、また、初期に対する4時間運転後の圧力損失上昇が40mmHgを超えてしまいエンジン負荷が大きくなったために、その時点で運転を取りやめた。

【0060】また、排気浄化装置の性能評価条件を、入口温度を300℃で5分保持し、更に400℃で2分間保持するパターンにかえた場合、5時間運転後の排気浄

化装置1によるPM及びNO_xの平均低減率は、PM除去率が91%、NO_x除去率が16%となり、これより、高温排気条件では特にNO_xの低減率が悪化することがわかる。本発明の排気浄化装置は、排気温度が350℃以下の条件で使用して効果が大きいので、排気温度の低い高効率の内燃機関の排気浄化に好適であることは明らかであるが、排気温度の高い内燃機関に対しても、配置位置を適宜選択することなどで温度条件を調整すれば対応可能となる。

10 【0061】以上のように、本発明の排気浄化装置を用いれば、200～350℃程度の比較的低排温条件の排気を高効率で浄化できるため、特別のエンジン制御法を用いなくても、容易にクリーン排気を実現できる。

【0062】次に、以下の実施例4～9及び比較例4～7では、本発明の排気浄化触媒、即ち、水素（H₂）生成触媒及び窒素酸化物（NO_x）浄化触媒を含んで成る排気浄化触媒について、性能評価試験を行った。

20 【0063】（実施例4）硝酸Fe水溶液を活性アルミナ粉末（平均粒子径1μm）に含浸し、乾燥後空气中400℃で1時間焼成して、Fe担持アルミナ粉末（粉末1）を得た。この粉末のFe濃度は2%であった。硝酸Rh水溶液を粉末1に含浸し、乾燥後、N₂中400℃で1時間焼成して、Rh及びFe担持アルミナ粉末（粉末2）を得た。この粉末のRh濃度は2%であった（Fe/Rhはモル比で0.54）。ジアトロジアミンPt水溶液を活性アルミナ粉末に含浸し、乾燥後空气中400℃で1時間焼成して、Pt担持アルミナ粉末（粉末3）を得た。この粉末のPt濃度は2%であった。

30 【0064】粉末3を70g、アルミナを70g、水140gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディライト質モノリス担体（1.3L、400セル）に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、コート層重量140g/L触媒担体（A）を得た。粉末2を70g、粉末3を70g、水140gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液を触媒担体（A）に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、総コート層重量280g/L触媒担体（B）を得た。触媒担体（B）に、酢酸Ba水溶液を酸化物換算で触媒1L当たり15g含浸担持させ、排気浄化触媒（C）を得た。

【0065】（実施例5）硝酸Feの代わりに硝酸Coを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た（Co/Rhはモル比で0.57）。

【0066】（実施例6）硝酸Feの代わりに硝酸Niを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た（Ni/Rhはモル比で0.57）。

【0067】（実施例7）硝酸Feの代わりに硝酸Mnを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た（Mn/Rhはモル比で0.53）。

【0068】（実施例8）実施例1とほぼ同様な操作、即ち、粉末2を70g、粉末3を140g、アルミナを70g、水280gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディライト質モノリス担体（1.3L、400セル）に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、コート層重量280g/L触媒担体（B）を得た。触媒担体（B）に、酢酸Ba水溶液を酸化物換算で触媒1L当たり15g含浸担持させ、排気浄化触媒（C）を得た。

【0069】（実施例9）活性アルミナの代わりに酸化ジルコニウムを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0070】（比較例4）硝酸Rh水溶液を活性アルミナ粉末（平均粒子径1μm）に含浸し、乾燥後、N₂中400℃で1時間焼成して、Rh担持アルミナ粉末（粉末4）を得た。この粉末のRh濃度は2%であった。ジエトログアミンPt水溶液を活性アルミナ粉末に含浸し、乾燥後空气中400℃で1時間焼成して、Pt担持アルミナ粉末（粉末3）を得た。この粉末のPt濃度は2%であった。粉末3を70g、アルミナを70g、水140gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディライト質モノリス担体（1.3L、400セル）に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、コート層重量140g/L触媒担体（A）を得た。粉末2を70g、粉末3を70g、水140gを磁性ボールミルに投入し、混合粉碎*

*してスラリー液を得た。このスラリー液を触媒担体（A）に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、総コート層重量280g/L触媒担体（B）を得た。触媒担体（B）に、酢酸Ba水溶液を酸化物換算で触媒1L当たり15g含浸担持させ、排気浄化触媒（C）を得た。

【0071】（比較例5）粉末1で、硝酸Feの濃度を0.2%にした以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0072】（比較例6）粉末1で、硝酸Feの濃度を40%にした以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0073】（比較例7）粉末1で、活性アルミナの粉末の平均粒子径を50μmにした以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0074】＜評価試験例＞

・耐久方法

排気量4400ccのエンジンの排気系に排気浄化触媒を装着し、前段の触媒入口温度を700℃とし、30時間運転した。

・評価方法

ディーゼルエンジンのエンジンの排気系に排気浄化触媒を装着し、触媒入口温度を300℃とし、15分間運転した。ガソリンエンジンの排気系に排気浄化触媒を取り付け、A/F=50、入口温度300℃とし、10分間運転した。なお、NO_x転化率は次の式

$$\text{NO}_x \text{ 転化率} = (1 - \text{触媒出口 NO}_x \text{ 量} / \text{触媒入口 NO}_x \text{ 量}) \times 100\%$$

により求めた。

【0075】

【表1】

	貴金属		元素		M/Rh(モル比)	Rh担持多孔質体種	多孔質体の粒子系
	Pt g/L	Rh g/L	M	g/L			
実施例4	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1μm
実施例5	2.8	1.4	Co	1.4	0.57	Al ₂ O ₃	1μm
実施例6	2.8	1.4	Ni	1.4	0.57	Al ₂ O ₃	1μm
実施例7	2.8	1.4	Mn	1.4	0.53	Al ₂ O ₃	1μm
実施例8	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1μm
実施例9	2.8	1.4	Fe	1.4	0.54	ZrO ₂	1μm
比較例4	2.8	1.4	なし	0	0.54	Al ₂ O ₃	1μm
比較例5	2.8	1.4	Fe	0.14	0.054	Al ₂ O ₃	1μm
比較例6	2.8	1.4	Fe	28.0	10.8	Al ₂ O ₃	1μm
比較例7	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	20μm

【0076】

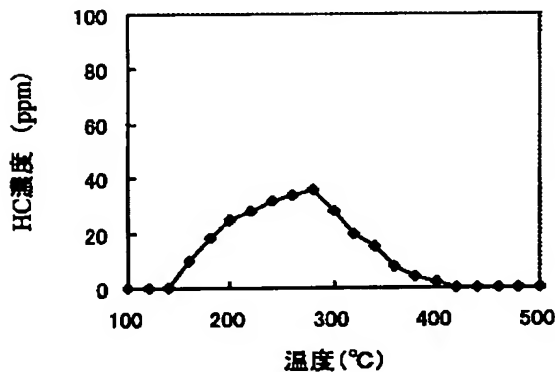
【表2】

	転化率% NO _x
実施例4	82
実施例5	80
実施例6	80
実施例7	77
実施例8	79
実施例9	80
比較例4	50
比較例5	60
比較例6	68
比較例7	68

【0077】表1及び表2に示すように、上記評価試験の結果、実施例4～9では、比較的低温な排気であってもNO_x転化率が良好であることがわかる。一方、比較例4～7では、NO_x転化率が悪いことがわかる。

【0078】以上、本発明を好適実施例及び比較例により詳細に説明したが、本発明はこれら実施例に限定されるものではなく、本発明の要旨の範囲内において種々の変形が可能である。例えば、本発明の触媒は、一体構造型担体に担持させて用いるのが望ましい。一体構造型担体としては、耐熱性材料からなるモノリス担体が望まし*

【図1】



*く、例えばコーディライトなどのセラミック製や、フェライト系ステンレスなどの金属製の担体を使用できる。また、触媒を担体上に塗り分けることで、NO_xとPMの排気浄化率を高めることができる。

【0079】

【発明の効果】以上説明してきたように、本発明によれば、PM中のC固体粒子（パーティキュレート粒子）を一旦炭化水素や水素に変換すること、触媒成分とPM粒子との接触（衝突）率を高めて該変換反応を促進させることとしたため、通常の燃焼条件の下で、特定の制御を必要とせずにNO_xとPMを連続的に自己浄化することが可能な排気浄化方法、排気浄化触媒及び排気浄化装置を提供することができる。

【図面の簡単な説明】

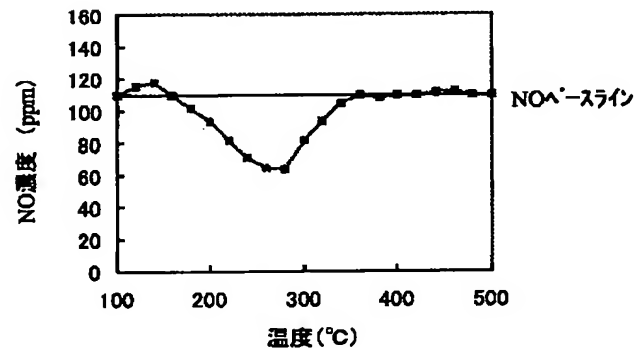
【図1】モデルガス評価試験によるCからのHC生成挙動を示すグラフである。

【図2】モデルガス評価試験によるNO_x還元浄化特性を示すグラフである。

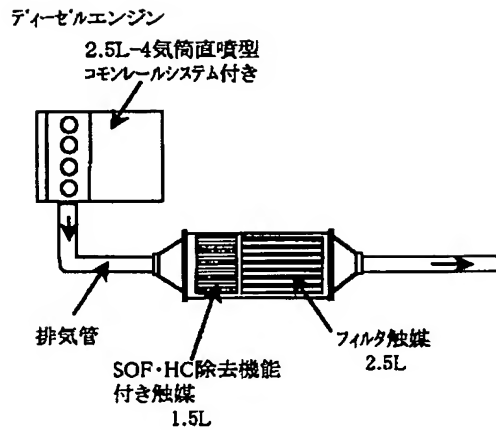
【図3】排気浄化装置の構成例を示す概略図である。

【図4】排気浄化装置の他の構成例を示す概略図である。

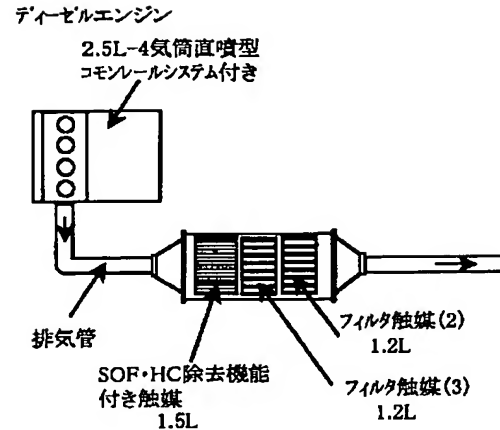
【図2】



【図3】



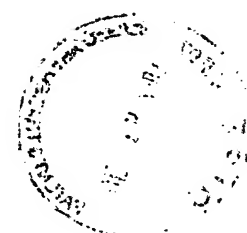
【図4】



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3/10			E
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BA12X BA28X BA30X BA31Y
BA33X BA36X BA37X BA38X
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FB23 FB30 FC08 ZA06A
ZA10A ZA10B ZA19A